DECLARATION

I, Mitsuru MAEDA, the translator of the attached document, do hereby certify that to the best of my knowledge and belief the attached document is a true English translation of Japanese Patent Application No. 2003-434900.

Signed, this 2nd day of June, 2006

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【Claim 1】

A carrier for latent electrostatic image development, comprising at least a core material and a cover layer, characterized in that the core material is a particulate ferrite comprising Zr in an amount of from 0.01 to 5% by mass and/or Bi in an amount of from 0.005 to 1% by mass.

【Claim 2】

The carrier for latent electrostatic image development according to claim 1, characterized in that particles of the core material comprise Fe in an amount of from 15 to 45% by mass, Mn in an amount of from 1 to 25% by mass, and Mg in an amount from 0.1 to 1.0% by mass.

【Claim 3】

A carrier for latent electrostatic image development, comprising at least a core material, and a cover layer, characterized in that the core material is a particulate ferrite comprising Zr in an amount of from 0.005 to 4% by mass and/or Bi in an amount of from 0.001 to 0.9% by mass.

【Claim 4】

The carrier for latent electrostatic image development according to claim 1, characterized in that particles of the carrier comprise Fe in an amount of from 10 to 40% by mass, Mn in an amount of from 1 to 25% by mass, and Mg in an amount from 0.1 to 1.0% by mass.

【Claim 5】

The carrier for latent electrostatic image development according to any one of claims 1 to 4, characterized in that the carrier particles have a magnetic moment of from 40 to 90 Am^2/kg at 1 kOe.

【Claim 6】

A carrier for latent electrostatic image development, comprising at least a core material, and a cover layer, characterized in that the core material is a particulate ferrite and the carrier comprises Zr in an amount of from 0.005 to 4% by mass and/or Bi in an amount of from 0.001 to 0.9% by mass, and has a magnetic moment of from 65 to 90 emu at 1 kOe, wherein the carrier has a dielectric breakdown voltage of not less than 1000 V, said dielectric breakdown voltage being determined by applying a direct-current voltage to the carrier using a measuring instrument having a rotary sleeve, in which a fixed magnet is set at a predetermined position, and an electrode set 1 mm apart from the sleeve.

【Claim 7】

A carrier for latent electrostatic image development, comprising at least a core material, and a cover layer, characterized in that the core material is a particulate ferrite, and the carrier comprises Zr in an amount of from 0.005 to 4% by mass and/or Bi in an amount of from 0.001 to 0.9% by mass and has a magnetic moment of from 65 to 90 emu at 1 kOe, wherein the carrier has a dielectric breakdown voltage of not less than 500 V, said dielectric breakdown voltage being determined with

a bridge measuring instrument by applying a direct-current voltage to the carrier particles, which achieve a chain state in a magnetic field of 1500 Gauss and which are present between electrodes set at an interval of 2 mm ± 0.3 mm.

【Claim 8】

The carrier for latent electrostatic image development according to claim 6 or 7, characterized in that particles of the carrier comprise Fe in an amount of from 10 to 40% by mass, Mn in an amount of from 1 to 25% by mass, and Mg in an amount from 0.1 to 1.0% by mass.

【Claim 9】

The carrier for latent electrostatic image development according to any one of claims 1 to 8, characterized in that the carrier has a weight-average particle diameter of from 20 to 65 μm, and includes particles having a particle diameter of not greater than 9 μm in an amount of not greater than 3.0% by weight.

【Claim 10】

The carrier for latent electrostatic image development according to any one of claims 1 to 9, characterized in that the cover layer comprises at least a silicone resin and/or an acrylic resin.

【Claim 11】

The carrier for latent electrostatic image development according to claim 10, characterized in that the cover layer comprises at least a silicone resin and an acrylic resin, wherein the acrylic resin is included in the cover layer in an amount of from 10% by weight to 90% by weight.

【Claim 12】

The carrier for latent electrostatic image development according to claim 10 or 11, characterized in that the cover layer has a layered structure such that each of the silicone

resin and the acrylic resin forms a layer.

【Claim 13】

A developer for latent electrostatic image development characterized by comprising a toner comprising at least a binder resin and a colorant, and a carrier for latent electrostatic image development according to any one of claims 1 to 12.

【Claim 14】

The developer for latent electrostatic image development according to claim 13, characterized in that the toner has a weight average particle diameter (Dw) of from 3 to 10 μm.

【Claim 15】

A container characterized by containing a developer for latent electrostatic image development according to claim 13 or 14.

【Claim 16】

An image forming method characterized by using a developer for latent electrostatic image development according to claim 13 or 14.

【Claim 17】

A process cartridge which comprises a photoconductor and at least one of charging means, developing means and cleaning means and which can be detachably set in a main body of an image forming apparatus while the photoconductor and at least the developing means are integrally supported, characterized in that the developing means bears a developer according to claim 13 or 14.

【Name of Document】 Specification

【Title of the Invention】 Carrier for latent electrostatic image development, developer, developer container, image forming method and process cartridge

【Technical Field】

【0001】

The present invention relates to a carrier which is used for developing a latent electrostatic image formed on a photoconductor by electrophotography or electrostatic recording to visualize the latent image; a developer containing the carrier and a toner; a container containing the developer; an image forming method using the developer; and a process cartridge bearing the developer.

【Background Art】

【0002】

In the past, an electrostatic or magnetic latent image is visualized by a toner in electrophotography apparatuses, electrostatic recording apparatuses, etc. For example, in electrophotography, an electrostatic image (a latent image) is formed on a photoconductor, and the latent image is then developed using a toner to form a toner image. The toner image is usually transferred to a transfer material such as paper, and subsequently fixed thereon by a method such as heating methods.

【0003】

In general, the toner used for electrostatic image development is a colored particulate material including a binder resin, and a colorant, a charge control agent and other additives, which are included in the binder resin. The method for manufacturing such a toner is broadly classified into a pulverization methods and suspension polymerization methods.

In the pulverization methods, toner is manufactured by melt-mixing a thermoplastic resin, a colorant, a charge control agent and an offset inhibitor, to uniformly disperse them in the thermoplastic resin, and then pulverizing the composition thus prepared, followed by classifying. By using such pulverization methods, toner having a certain level of characteristics can be manufactured, but the materials which

can be used for manufacturing the toner are limited.

【0004】

For example, the composition prepared by melt-mixing must be a material which can be pulverized and classified by an economically viable apparatus. In order to fulfill this requirement, the composition prepared by melt-mixing has to be sufficiently brittle to be pulverized and classified.

When the composition is actually pulverized to prepare particles, the particles tend to have a wide particle size distribution. If it is attempted to obtain a copy image with good resolution and gradation using such particles, fines particles with a particle size of, for example, 5 μm or less and coarse particles of 20 μm or more must be removed from the particles. Therefore, the toner yield becomes very low. In addition, additives such as a coloring agent and a charge control agent cannot be uniformly dispersed in a thermoplastic resin when the pulverization methods are used. Unevenly dispersed components adversely affect the fluidity, developing property, durability, and image quality of the resultant toner.

【0005】

Recently, in order to solve the problem caused by such pulverization methods, it has been proposed to manufacture toner by polymerization methods such as suspension polymerization methods. These methods are now being used. Such toner particles for electrostatic image development are prepared, for example, by suspension polymerization methods. However, the toner particles obtained by suspension polymerization methods are spherical, and therefore the resultant toner has poor cleaning property. In development and transfer of an image with a low image occupancy, the amount of residual toner particles after transfer is small and therefore defective cleaning is not caused. However, in development and

transfer of an image with a high image occupancy such as photograph images or in a case where toner particles constituting an image are not transferred due to paper feed failure or the like, toner particles remain on the photoconductor. If the toner particles are accumulated, background fouling is caused. In addition, such a residual toner is deposited on a charger roller for contact-charging the photoconductor and other members, thus reducing the inherent charging ability thereof.

【0006】

To solve these problems, a method in which fine resin particles prepared by emulsion polymerization are associated to prepare toner particles having irregular forms is disclosed (Japanese Patent No. 2537503).

However, even if the toner particles obtained by an emulsion polymerization method are subjected to a water rinsing treatment, a surfactant remains not only on the surface of the particles but also in the internal portion thereof, and therefore the environmental stability of the charge property of the toner deteriorates. In addition, the toner has a broad charge distribution, and therefore the resultant image has background fouling. Moreover, the remaining surfactant also contaminates a photoconductor, a charge roller, a developing roller, etc., thereby deteriorating their original charging ability.

【0007】

Toner particles used for an image-fixing process, in which an image is fixed by contact heating using a heating member such as heating rollers, are required to have satisfactory releasability from the heating member (hereinafter referred to as "offset resistance"). The offset resistance can be improved by arranging a release agent on the surface of toner particles.

Published unexamined Japanese Patent Applications Nos. 2000-292973 and 2000-292978 have proposed techniques such that fine resin particles are contained in toner particles and in addition the resin particles are unevenly located on the surface of the toner particles to improve the offset resistance of the toner. However, the techniques cause increase of lowest fixable temperature, and therefore the toner has insufficient low temperature fixability, i.e., insufficient energy saving property.

【0008】

The methods, in which toner particles having irregular forms are prepared by associating resin particles prepared by emulsion polymerization, have the following disadvantages. When particles of a release agent are associated to improve the offset resistance of the toner, the release agent particles are included inside the toner particles, and thereby the offset resistance of the toner cannot be improved satisfactorily. In addition, since resin particles, release agent particles and coloring agent particles are randomly mixed and fused to form toner particles, the composition of the toner particles varies (i.e., contents of the toner constituents in the toner particles vary) and further properties such as molecular weight of the binder resin in the toner particles vary. As a result, the individual toner particles have different surface properties, and therefore the toner cannot stably produce good images over a long period of time. Furthermore, in an image forming system which requires the toner to have a low temperature fixability, defective fixing is caused due to the fine resin particles unevenly located on the surface of the toner, and therefore the toner does not have a desired fixable temperature range.

【0009】

Developing methods for use in electrophotography are

roughly classified into one-component developing methods using a toner alone as a main component and two-component developing methods using a mixture of a toner and a non-coat carrier such as glass beads and magnetic particles or a coated carrier whose surface is coated with a resin.

Since the two-component developing methods use a carrier, which has so wide surface area as to well frictionally charge toner, the toner has relatively stable charging properties compared to toner used for the one-component developing methods. Therefore, the methods have an advantage in that high-quality images are produced over a long period of time. In addition, the two-component developing methods are superior in ability to feed the toner to a developing region, and are often used for high-speed machines.

Since the two-component developing methods have such advantages, the methods are also widely employed for digital electrophotographic systems in which a latent electrostatic image formed on a photoconductor using laser beams, etc. is developed to be visualized.

【0010】

Recently, it is desired to produce images with higher resolution and higher highlight reproducibility or to produce color images and therefore it is attempted to decrease the size of a minimum unit (one dot) of latent images and to increase the dot density. Particularly, a strong need exists for a developing system that can develop these latent images (dots) with high reproducibility. To satisfy the need, various proposals have been made on process conditions and developers (toners and carriers). With respect to process conditions, proposals such as formation of a smaller developing gap, a photoconductor having a thin layer, and writing light beams having a smaller diameter are effective. However, these

techniques increase the cost and still have a big problem to be solved with respect to reliability, etc.

【0011】

With respect to developers, the use of a toner having a small particle diameter significantly improves the reproducibility of dots. However, developers containing such a toner with a small particle diameter have problems to be solved in that background fouling occurs and image density is low. A full-color toner with a small particle diameter uses a resin with low softening point to produce images with sufficient color tone but forms a relatively large amount of spent toner on the carrier compared to a black toner, thus deteriorating the developer and often causing scattering of toner particles and background fouling.

【0012】

Various proposals have been made on the use of carriers with a small particle diameter. The carriers with a small particle diameter have the following advantages.

(1) These carriers have a large surface area and can thereby impart sufficient charges to individual toner particles by friction, thus avoiding formation of toner particles with a low charge quantity or with an opposite charge. As a result, background fouling is hardly caused and dot images with good reproducibility can be produced with hardly causing scattering and bleeding around the dot images.

(2) These carriers have a large surface area and can prevent occurrence of background fouling. Therefore, even when the average charge quantity of the toner is decreased, images with sufficient image density can be produced. Accordingly, carriers with a small particle diameter can remedy the drawbacks of the toners with a small particle diameter and are preferably used for enhancing the advantages of the toner with a small

particle diameter.

(3) The carriers with a small particle diameter can form dense magnetic brush with good fluidity, thus preventing formation of traces or marks of the magnetic brush on images.

【0013】

As mentioned above, carriers with a small particle diameter have been used because of having the above-mentioned advantages. In addition, the materials used as the core materials of carriers have been changed to reduce loads on the environment. Specifically, Cu-Zn ferrites, which have been often used for a core material, are now hardly used, because of using metal elements such as copper and zinc. Instead of the Cu-Zn ferrites, Mn ferrites are now often used. Mn ferrites include various additives to improve their properties and Mg is often used as an additive. For example, Japanese Patent No. 3243376 (patent document No. 1) discloses a technique in that Mg and Sr are added to a Mn ferrite to reduce variation in magnetization among carrier particles. Thus, various improvements have been made on Mn ferrites with increasing use thereof, thereby improving their quality. However, Mn ferrites have a problem to be solved in that when the magnetic properties of Mn ferrites are controlled so as to fall within regular usable regions, the ferrites have a low resistance and form defective images such as halftone images with uneven image density.

【0014】

Conventional carriers with a small particle diameter often cause adhesion of carrier particles (or scattering of carrier particles), which is a big problem to be solved because of damaging the photoconductor or fixing roller. Therefore, it is difficult to practically use such carriers.

To solve these problems, the patent document No. 1 proposes

a specific carrier which has a volume-average particle diameter of 25 to 45 μm and contains particles with a particle diameter of not greater than 22 μm in an amount of not greater than 1% and which has a magnetization of 67 to 88 emu/g in a magnetic field of 1 kOe, wherein scattered particles have a magnetization 10 emu/g lower than the inherent magnetization. This technique tends to improve the carrier adhesion. As a result of the present inventors' evaluation test, abnormal images "rough image" (images with different density spots) were frequently produced when analogue halftone images were produced using a developing method in which a direct-current voltage superimposed with an alternating-current voltage is used as the developing bias. Analogue halftone images were produced in this evaluation test to simulate digital images with high precision of 1200 dpi or more, and the test is a severe test aiming at formation of next-generation digital images with higher precision. In contrast, digital images having such a low resolution as 400 dpi hardly cause the rough image problem.

【0015】

Published unexamined Japanese Patent Application No. 2002-296846 (patent document No. 2) proposes a technique in that the particle diameter of carrier is decreased to uniformize halftone images. The abnormal halftone images described in the patent document No. 2 is considered to be caused by variation of particle diameters. In contrast, the concern in the present invention is abnormal halftone images caused by electrical factors as mentioned below. To verify the difference therebetween, the present inventors have examined on the machine CF-70 (available from Konica Minolta Business Technologies, Inc.) used as an evaluation machine in the patent document No. 2. As a result thereof, it was found that CF-70 is a full-color copier with a resolution of 400 dpi, and abnormal

halftone images which are a problem to be solved by the present invention cannot be produced.

【0016】

Generally, when resolution of digital images is increased, an input image can be reproduced with better reproducibility. This is also true for electrophotography, and investigations on images with higher resolution of not less than 1200 dpi, which is higher than that (400dpi) of the conventional digital images, have revealed that images having smooth highlight portions or halftone density portions can be produced thereby.

However, production of images while merely increasing resolution is insufficient to produce high quality images, and individual dots constituting the images must have high dot uniformity. The term "good dot uniformity" used herein means that variation in the amount of toner constituting each dot image is little. In an image with a higher resolution, the amount of toner constituting each dot is smaller than that in an image with a lower resolution because the dot has a smaller diameter. Targeted high-quality images with smooth entire appearance can be obtained by uniformizing the amount of toner constituting each dot. However, in this case, if the amount of toner constituting each dot largely varies, images with uneven densities are formed due to the variation of the amount of the toner. In this connection, images with a lower resolution seem to have less density irregularity because each dot in the low resolution images bears a larger amount of toner. Therefore, recently investigations have been made to improve the dot uniformity of individual dot images to produce high-quality images with higher resolution.

【0017】

The "roughness" which is evaluated in the present invention is a phenomenon in which images with highlight to

halftone images have uneven densities, i.e., roughness in density and which is caused by deterioration of the dot uniformity mentioned above. A rough image is an abnormal image which is easily formed in images with high resolution. The analogue halftone image used for evaluation in the present invention corresponds to an output image with the highest resolution. If the roughness can be improved in analogue halftone images, formation of high-quality images with high resolution can be realized.

【0018】

The copier CF-70 is a machine for producing images with a resolution of 400 dpi (one dot: about 60 μm) and therefore does not produce rough images because of having a relatively low resolution. More specifically, the abnormal halftone images discussed in patent document No. 2 are caused by the variation in particle diameter. In the machine used in the patent document No. 2, the abnormal half tone images, which are a problem to be solved in the present invention and which is caused by an electrical factor, are not produced. Namely, the abnormal halftone images caused by electrical factors are a new problem to be solved in the present invention, and are not described in the patent document No. 2. A copier which produces analogue half tone images is used for the present invention to simulate a copier with high resolution. Therefore, even when the carrier described in the patent document No. 2 is used for the present invention, the object of the present invention cannot be attained.

【0019】

Since ferrite carriers such as Ni-Zn ferrites, Mn-Zn ferrites or Cu-Zn ferrites have a dielectric breakdown voltage of 1000 V or more, leakage of the potential of a latent electrostatic image formed on a photoconductor to the carrier

during development is not caused, and therefore streak images, etc. are not caused. However, these ferrite carriers have an excessively high density. In order to remedy the drawback, published unexamined Japanese Patent Application No. 07-225497 (patent document No. 3) discloses use of a Li-Fe ferrite containing lithium oxide in an amount of 17.0 to 29.0% by mole based on Fe_2O_3. In addition, it is described therein that such a Li ferrite has a saturation magnetization of about 43 to 70 emu/g. Further, it is described in the examples therein that the magnetic field applied is 3000 Oe, and the maximum saturation magnetization is 62 in the examples and comparative examples in the publication. It is highly possible that the ferrite disclosed in the patent document No. 3 will have a saturated magnetization of less than 70 emu/g if the saturation magnetization is determined at 1000 Oe. Accordingly, this ferrite is not a high-magnetized ferrite used for the present invention and is a low-magnetized ferrite.

【0020】

It is described in published unexamined Japanese Patent Application No. 11-202559 (patent document No. 4) to use a ferrite containing MoO in an amount of 5 to 35% by mole, MgO in an amount of 10 to 45% by mole and Fe_2O_3 in an amount of 45 to 55% by mole to avoid a problem in that properties of a Li-Fe ferrite often vary because the Li component is susceptible to humidity and temperature. However, this Li-Fe ferrite described in the patent document No. 4 is a low magnetization ferrite because the saturation magnetization thereof is different from that of the ferrite used for the present invention. With respect to the electric properties, a current at a voltage of 250V is described in the patent document. However, in order to solve the problem to be solved in the present invention, it is important to evaluate the electric properties

using the measuring methods specified in the present application.

【0021】

Published unexamined Japanese Patent Applications Nos. 06-35230 and No. 06-51563 (patent documents Nos. 5 and 6) disclose carriers including a ferrite as a main component and having specific average particle diameter, bulk density and intensity of magnetization. However, these carriers are mainly intended to prevent adhesion or deposition of carrier particles to a latent electrostatic image bearing member (such as photoconductors) and do not have a sufficient resistance to be used as a carrier.

【0022】

【Patent document No. 1】 Japanese Patent No. 3243376

【Patent document No. 2】 Published unexamined Japanese Patent Application No. 2002-296846

【Patent document No. 3】 Published unexamined Japanese Patent Application No. 7-225497

【Patent document No. 4】 Published unexamined Japanese Patent Application No. 11-202559

【Patent document No. 5】 Published unexamined Japanese Patent Application No. 6-35230

【Patent document No. 6】 Published unexamined Japanese Patent Application No. 6-51563

【Disclosure of the present Invention】

【Problem to be Solved by the Invention】

【0023】

The present invention is made to solve the problems mentioned above. An object of the present invention is to provide a carrier and a developer for electrostatic development, which have a sufficient resistance even when the magnetic properties thereof are set to fall within regular usable regions

and which do not produce abnormal half tone images with uneven densities due to low resistance of the carrier used.

In addition, the object of the present invention is to provide a carrier and developer for electrostatic development, which does not lose advantages of carrier with a small particle diameter and does not cause carrier adhesion and which can produce halftone images without roughness and character images with good reproducibility while being capable of stably maintaining their charges over a long period of time.

Further, the object of the present invention is to provide a container containing the above-mentioned developer, an image forming method using the developer and a process cartridge bearing the developer.

【Solution for Solving the Problem】

【0024】

According to the present invention, the following (1) to (17) is provided.

(1) A carrier for latent electrostatic image development, which includes at least a core material, and a cover layer and which is characterized in that the core material is a particulate ferrite including Zr in an amount of from 0.01 to 5% by mass and/or Bi in an amount of from 0.005 to 1% by mass.

(2) The carrier for latent electrostatic image development recited in paragraph (1), which is characterized in that particles of the core material include Fe in an amount of from 15 to 45% by mass, Mn in an amount of from 1 to 25% by mass, and Mg in an amount from 0.1 to 1.0% by mass.

(3) A carrier for latent electrostatic image development, which includes at least a core material, and a cover layer and which is characterized in that the core material is a particulate ferrite including Zr in an amount of from 0.005 to 4% by mass and/or Bi in an amount of from 0.001 to 0.9% by mass.

(4) The carrier for latent electrostatic image development recited in paragraph (1), which is characterized in that particles of the carrier include Fe in an amount of from 10 to 40% by mass, Mn in an amount of from 1 to 25% by mass, and Mg in an amount from 0.1 to 1.0% by mass.

(5) The carrier for latent electrostatic image development recited in any one of paragraphs (1) to (4), which is characterized in that the carrier particles have a magnetic moment of from 40 to 90 Am^2/kg at 1 kOe.

(6) A carrier for latent electrostatic image development, which includes at least a core material, and a cover layer and which is characterized in that the core material is a particulate ferrite, and the carrier includes Zr in an amount of from 0.005 to 4% by mass and/or Bi in an amount of from 0.001 to 0.9% by mass and has a magnetic moment of from 65 to 90 emu at 1 kOe, wherein the carrier has a dielectric breakdown voltage of not less than 1000 V, wherein the dielectric breakdown voltage is determined by applying a direct-current voltage to the carrier using a measuring instrument having a rotary sleeve, in which a fixed magnet is set at a predetermined position, and an electrode set 1 mm apart from the sleeve.

(7) A carrier for latent electrostatic image development, which includes at least a core material, and a cover layer and which is characterized in that the core material is a particulate ferrite, and the carrier includes Zr in an amount of from 0.005 to 4% by mass and/or Bi in an amount of from 0.001 to 0.9% by mass and has a magnetic moment of from 65 to 90 emu at 1 kOe, wherein the carrier has a dielectric breakdown voltage of not less than 500 V, wherein the dielectric breakdown voltage is determined with a bridge measuring instrument by applying a direct-current voltage to the carrier particles, which achieve a chain state in a magnetic field of 1500 Gauss and which are

present between electrodes set at an interval of 2 mm ± 0.3 mm.
(8) The carrier for latent electrostatic image development recited in paragraph (6) or (7), which is characterized in that the carrier particles include Fe in an amount of from 10% by mass to 40% by mass, Mn in an amount of from 1 to 25% by mass, and Mg in an amount from 0.1 to 1.0% by mass.
(9) The carrier for latent electrostatic image development recited in any one of paragraphs (1) to (8), which is characterized in that the carrier has a weight-average particle diameter of from 20 to 65 μm, and includes particles having a particle diameter of not greater than 9 μm in an amount of not greater than 3.0% by weight.
(10) The carrier for latent electrostatic image development recited in any one of paragraphs (1) to (9), which is characterized in that the cover layer includes at least a silicone resin and/or an acrylic resin.
(11) The carrier for latent electrostatic image development recited in paragraph (10), which is characterized in that the cover layer includes at least a silicone resin and an acrylic resin, wherein the acrylic resin is included in the cover layer in an amount of from 10% by weight to 90% by weight.
(12) The carrier for latent electrostatic image development recited in paragraph (10) or (11), which is characterized in that the cover layer has a layered structure such that each of the silicone resin and the acrylic resin forms a layer.
(13) A developer for latent electrostatic image development characterized by including a toner including at least a binder resin and a colorant, and a carrier for latent electrostatic image development recited in any one of paragraphs (1) to (12).
(14) The developer for latent electrostatic image development recited in paragraph (13), which is characterized in that the toner has a weight average particle diameter (Dw) of from 3 to

10 μm.

(15) A container characterized by containing a developer for latent electrostatic image development recited in paragraph (13) or (14).

(16) An image forming method characterized by using a developer for latent electrostatic image development recited in paragraph (13) or (14).

(17) A process cartridge which includes a photoconductor and at least one of charging means, developing means and cleaning means and which can be detachably set in a main body of an image forming apparatus while the photoconductor and at least the developing means are integrally supported and which is characterized in that the developing means bears a developer recited in paragraph (13) or (14).

【Effects of the present Invention】

【0025】

The carrier and the developer for electrostatic development of the present invention do not lose the advantages of carrier having a small particle diameter; can produce halftone images without roughness; do not cause carrier adhesion; can reproduce images without roughness while preventing occurrence of carrier adhesion; can produce character images with good reproducibility; and can stably maintain their charges over a long period of time. Therefore, good images can be formed not only at an initial stage but also after a number of copies are produced.

In addition, the present invention provides a container containing the above-mentioned developer; an image forming method using the above-mentioned developer; and a process cartridge bearing the above-mentioned developer.

【Most preferable Embodiment of the present Invention】

【0026】

Hereinafter, the present invention will be specifically explained.

(I) As a result of intensive investigations of the present inventors to solve the above-mentioned problems of the conventional technologies, it is found that the problems of the conventional technologies can be effectively solved by a carrier which includes at least a core material and a cover layer, wherein the core material is a particulate ferrite containing Zr in an amount of 0.01 to 5% by mass. This is because the resistance of the carrier can be increased without decreasing its magnetic moment by including Zr therein. When the content is less than 0.01% by mass, the effect can be hardly produced because the content is too low. Therefore, it is not preferable. In contrast, when the content is greater than 5% by mass, adverse effect of decreasing the magnetic moment is produced because the content of Zr is too high. Therefore, it is not preferable.

【0027】

In addition, it is found that when a carrier, which includes a particulate ferrite as a core material and a cover layer, includes Bi in an amount of from 0.005 to 1% by mass, a noticeable improvement effect can be produced. This is because the resistance of the carrier can be increased without decreasing its magnetic moment by including Bi therein similarly to the case where Zr is included therein. When the content is less than 0.005% by mass, the effect can be hardly produced because the content is too low. Therefore, it is not preferable. In contrast, when the content is greater than 1% by mass, adverse effect of decreasing the magnetic moment is produced because the content of Zr is too high. Therefore, it is not preferable.

【0028】

Further, it is found that when a carrier, which includes

a particulate ferrite as a core material and a cover layer, includes Zr in an amount of 0.01 to 5% by mass and Bi in an amount of from 0.005 to 1% by mass, a noticeable improvement effect can be produced. This is because a synergy effect of Zr and Bi is produced.

【0029】

Furthermore, when the particles of the core material include Fe, Mn and Mg in amounts of 15 to 45% by mass, 1 to 25% by mass, and 0.1 to 1.0% by mass, respectively, a noticeable improvement effect can be produced. This is because by balancing the contents of Fe, Mn and Mg so as to fall in the respective ranges, the resultant ferrite has a good combination of magnetic moment and resistance. When the contents do not fall within the ranges, the good combination properties cannot be imparted thereto because the balance of the contents is disturbed.

【0030】

In addition, as a present inventors' investigation to solve the above-mentioned problems of the conventional technologies, it is found that the above-mentioned problems of the conventional carriers can be well solved by a carrier containing a core material and a cover layer, wherein the core material is a particulate ferrite containing Zr in an amount of 0.005 to 4% by mass and/or Bi in an amount of 0.001 to 0.9% by mass.

This is because by including Zr and/or Bi therein, the resistance of the carrier can be increased without decreasing the magnetic moment thereof. When the content of Zr is less than 0.005% by mass, the effect can be hardly produced because the content is too low. Therefore, it is not preferable. In contrast, when the content is greater than 4% by mass, adverse effect of decreasing the magnetic moment is produced because

the content of Zr is too high. Therefore, it is not preferable.

【0031】

The same is true for Bi. Specifically, when the content of Bi is less than 0.001% by mass, the effect can be hardly produced because the content is too low. Therefore, it is not preferable. In contrast, when the content is greater than 0.9% by mass, adverse effect of decreasing the magnetic moment is produced because the content of Bi is too high. Therefore, it is not preferable. In addition, because of having a low melting point, Bi has an effect of producing particles with good shape and smooth surface. Although the added amount of Bi is small as mentioned above, the effect can be fully produced. When the content of Bi is less than 0.001% by mass, the effect can be hardly produced because the content is too low. Therefore, it is not preferable. In contrast, when the content is greater than 0.9% by mass, the resultant particles become too soft in a granulation process. Therefore, the shape and surface conditions of the carrier cannot be controlled at the same time. Therefore, it is not preferable.

【0032】

By including both Zr and Bi therein, synergy therebetween can be produced. Specifically, carrier particles which have an excellent combination of magnetic moment and resistance while having good particle shape and good surface conditions can be produced. Therefore, it is more preferable.

【0033】

When the above-mentioned carrier particles of the carrier for latent electrostatic image development include Fe, Mn and Mg in amounts of 10 to 40% by mass, 1 to 25% by mass, and 0.1 to 1.0% by mass, respectively, a noticeable improvement effect can be produced. This is because when the contents of Fe, Mn and Mg are thus balanced, carrier particles having good

properties such as good combination of magnetic moment and resistance can be provided. When the contents do not fall in the ranges, the balance is disturbed, and thereby the good combination properties cannot be imparted thereto. Therefore, it is not preferable.

【0034】

Further, a carrier for latent electrostatic image development which has a weight average particle diameter of from 20 to 65 μm while including particles having a particle diameter of not greater than 9 μm in an amount of not greater than 3.0% by weight and which has a magnetic moment of from 40 to 90 Am^2/kg at 1 kOe can further enhance the improvement effect.

【0035】

With respect to the particle diameter, when the particle diameter is less than 20 μm, uniformity of the particles deteriorates and thereby carrier adhesion is caused. Therefore, it is not preferable. In contrast, when the particle diameter is greater than 65 μm, reproducibility of fine images deteriorates, i.e., images with good fineness cannot be formed. Therefore, it is not preferable. When the content of particles having a diameter of not greater than 9 μm is greater than 3.0% by weight, uniformity of the carrier particles deteriorates and thereby carrier adhesion is caused, similarly to the case where the weight average particle diameter is less than 20 μm.

When the magnetic moment is controlled so as to fall within the range, the holding power between carrier particles can be controlled so as to be in a proper range and therefore toner can be rapidly dispersed (or mixed) in the carrier or developer. However, when the magnetic moment is less than 40 Am^2/kg at 1 kOe, carrier adhesion is caused because the magnetic moment is too low. Therefore, it is not preferable.

In contrast, when the magnetic moment is greater than 90

Am^2/kg at 1 kOe, the brush of the developer formed in a developing process become too hard, and thereby reproducibility of fine images is deteriorated, i.e., images with good fineness cannot be produced. Therefore, it is not preferable.

【0036】

(II) As a result of the present inventors' investigation to solve the problems of the conventional technologies, it is found that the above-mentioned problems of the conventional technologies can be efficiently solved by a carrier for latent electrostatic image development, which includes at least a core material, and a cover layer and which is characterized in that the core material is a particulate ferrite, and the carrier includes Zr in an amount of from 0.005 to 4% by mass and/or Bi in an amount of from 0.001 to 0.9% by mass and has a magnetic moment of from 65 to 90 emu at 1 kOe, wherein the carrier has a dielectric breakdown voltage of not less than 1000 V, wherein the dielectric breakdown voltage is determined by applying a direct-current voltage to the carrier using a measuring instrument having a rotary sleeve, in which a fixed magnet is set at a predetermined position, and an electrode set 1 mm apart from the sleeve.

【0037】

(III) As a result of the present inventors' investigation to solve the problems of the conventional technologies, it is found that the above-mentioned problems of the conventional technologies can be efficiently solved by a carrier for latent electrostatic image development, which includes at least a core material, and a cover layer and which is characterized in that the core material is a particulate ferrite, and the carrier includes Zr in an amount of from 0.005 to 4% by mass and/or Bi in an amount of from 0.001 to 0.9% by mass and has a magnetic moment of from 65 to 90 emu at 1 kOe, wherein the carrier has

a dielectric breakdown voltage of not less than 500 V, wherein the dielectric breakdown voltage is determined with a bridge measuring instrument by applying a direct-current voltage to the carrier particles, which achieve a chain state in a magnetic field of 1500 Gauss and which are present between electrodes set at an interval of 2 mm ± 0.3 mm.

【0038】

By including Zr and/or Bi, the dielectric breakdown voltage can be increased without decreasing the magnetic moment of the carrier. When the content of Zr is less than 0.005% by mass, the effect thereof is hardly produced. Therefore, it is not preferable. In contrast, when the content of Zr is too high, the magnetic moment is decreased. Therefore, it is not preferable.

【0039】

The same is true for Bi. Specifically, when the content of Bi is less than 0.001% by mass, the effect can be hardly produced because the content is too low. Therefore, it is not preferable. In contrast, when the content is greater than 0.9% by mass, adverse effect of decreasing the magnetic moment is produced because the content of Bi is too high. Therefore, it is not preferable. In addition, because of having a low melting point, Bi has an effect of producing particles with good shape and smooth surface. Although the added amount of Bi is small as mentioned above, the effect can be fully produced. When the content of Bi is less than 0.001% by mass, the effect can be hardly produced because the content is too low. Therefore, it is not preferable. In contrast, when the content is greater than 0.9% by mass, the resultant particles become too soft in a granulation process. Therefore, the shape and surface conditions of the carrier cannot be controlled at the same time. Therefore, it is not preferable.

【0040】

In this regard, Zr and Bi are used by themselves or compounds thereof are used. It is more preferable to use compounds thereof. Suitable materials for use as the compounds include oxides and carbides thereof.

【0041】

When the magnetic moment is controlled so as to fall within the range, the holding power between carrier particles can be controlled so as to fall in a proper range and therefore toner can be rapidly dispersed (or mixed) in the carrier or developer. However, when the magnetic moment is less than 65 Am^2/kg at 1 kOe, carrier adhesion is caused because the magnetic moment is too low. Therefore, it is not preferable.

In contrast, when the magnetic moment is greater than 90 Am^2/kg at 1 kOe, the brush of the developer formed in a developing process become too hard, and thereby reproducibility of fine images is deteriorated, i.e., images with good fineness cannot be produced. Therefore, it is not preferable.

【0042】

With respect to the dielectric breakdown voltage as determined in paragraph (II), it is found that the degree of roughness of images is correlated with the dielectric breakdown voltage, which is determined by applying a direct-current voltage to the carrier using a measuring instrument having a rotary sleeve containing a fixed magnet at a predetermined position thereof and electrodes set 1 mm apart from the sleeve. A carrier having a dielectric breakdown voltage of not less than 1000 V, which is determined by the above method, can produce images with less roughness. The reason therefor is considered to be that a carrier having a lower dielectric breakdown voltage can cause a larger leakage in development, thereby producing latent electrostatic images with deteriorated properties. The

carrier having a dielectric breakdown voltage of 1000 V or more, which is determined by the above method, also has a higher margin of carrier adhesion. This is because in a carrier having a lower dielectric breakdown voltage, charges are often formed in its core material, thereby easily causing carrier adhesion. The degree of carrier adhesion tends to increase as the linear velocities of the photoconductor and the development sleeve increase.

The dielectric breakdown voltage as used herein is defined as a voltage at which the resistance of the carrier rapidly drops, i.e., at which an excess current rapidly flows in the carrier. Namely, the dielectric breakdown voltage is defined as a voltage at which a large current suddenly flows because the carrier cannot resist to the applied voltage, although only a small amount of current flows in the carrier until then.

【0043】

With respect to the dielectric breakdown voltage mentioned above in paragraph (III), it is found that the degree of roughness of images is correlated with the dielectric breakdown voltage, which is determined by applying a direct-current voltage to chains of the carrier particles formed in a gap between electrodes in a magnetic field of 1500 Gauss. Specifically, when the carrier has a dielectric breakdown voltage of 500 V or more, which is determined using a bridge measuring instrument and electrodes having a distance of 2 ± 0.3 mm, the roughness of images can be improved. This is probably because a carrier having a lower dielectric breakdown voltage can cause a larger leakage in development, thereby producing latent electrostatic images with deteriorated properties. In addition, a carrier having a dielectric breakdown voltage of 500 V or more, which is determined using a bridge measuring instrument and electrodes having a distance

of 2 ± 0.3 mm, also has a wider margin of carrier adhesion. This is because a carrier having a lower dielectric breakdown voltage can often induce charges in its core material, thereby often causing carrier adhesion. The degree of carrier adhesion is heightened with increase of the linear velocities of the photoconductor and the development sleeve. As mentioned above, the dielectric breakdown voltage as used herein is defined as a voltage at which the resistance of the carrier rapidly drops, i.e., an excess current rapidly flows in the carrier. It is important that the resistance should be determined with a bridge measuring instrument such as a resistance measuring instrument as described in published unexamined Japanese Patent Application No. 07-225497, and it is more important to use a bridge measuring instrument in which the distance between electrodes is 2 ± 0.3 mm. If a dielectric breakdown voltage is determined with the measuring instrument as described in published unexamined Japanese Patent Application No. 07-225497 in which the distance between electrodes is 6.5 mm, the measured dielectric breakdown voltage is not correlated with the degree of roughness of images. This is probably because, as the distance between electrodes decreases, a current can flow more easily, and therefore the dielectric breakdown voltage can be determined with an increased sensitivity.

【0044】

Further, in the cases of paragraphs (II) and (III), it is very preferable to use a combination of Zr and Bi because the effects thereof can be synergistically enhanced and therefore the resultant carrier has high levels of magnetic moment and resistance, while being superior in particle shape and surface conditions of particles.

【0045】

In addition, in the cases of paragraphs (II) and (III),

the core material of the carrier preferably includes Fe, Mn and Mg in amounts of from 10 to 40% by mass, from 1 to 25% by mass, and from 0.1 to 1.0% by mass, respectively, to enhance the improvement effect. By including Fe, Mn and Mg in the above-specified amounts, the ferrite core material can have well-balanced magnetic moment, resistance and other properties. If the contents are out of the above-specified ranges, the ferrite core particle cannot have such well-balanced properties. Therefore it is not preferable.

【0046】

In addition, in these cases, it is preferred that the carrier for latent electrostatic image development has a weight-average particle diameter of 20 to 65 μm, and the content of carrier particles having a particle diameter of 9 μm or less is 3.0% by weight or less, to enhance the improvement effect. Carrier particles having a weight-average particle diameter less than 20 μm may have low uniformity. In addition, since the average particle diameter is small, the magnetization of each particle shifts to a lower side, and the number of particles with low magnetization increases, resulting in occurrence of carrier adhesion. Therefore, it is not preferable. In contrast, carrier particles having a weight-average particle diameter exceeding 65 μm produce fine images with poor reproducibility, i.e., cannot produce fine images with good fineness. Therefore, it is not preferable. Carrier particles containing particles having a particle diameter of 9 μm or less in an amount of greater than 3.0% by weight include non-uniform particles and have a larger number of lowly magnetized particles, resulting in occurrence of carrier adhesion, similarly to the above-mentioned case where the carrier particles have a weight-average particle diameter of less than 20 μm.

【0047】

The term "% by mass" used herein means percentages of an element on the basis of the atomic weight of the element, and is generally used for elementary analysis. Therefore, "% by mass" is substantially equivalent to "% by weight".

【0048】

Next, the method for manufacturing the core material will be explained.

At first, raw materials for a ferrite are weighed so as to have the predetermined weights, and they are mixed with a proper amount of water. The mixture is dispersed for 0.5 to 24 hours using a disperser such as ball mills or vibration mills to prepare a slurry. The slurry is then dried, pulverized and pre-baked at a temperature of from 500 to 1500℃. The pre-baked material is further pulverized in a ball mill to prepare a powder having a particle diameter suitable for preparing the target core material. The thus pulverized material is then mixed with water, a binder resin, and optional additives, followed by granulation by spray drying. The granules are baked at a temperature of from 800 to 1600℃, followed by pulverization and classification to prepare particles with a target particle diameter distribution. If desired, the surface of the particles may be re-oxidized. However, in the present invention, the preparation method is not limited to the above method.

【0049】

In addition, by using at least one or preferably both of a silicone resin and an acrylic resin for the cover layer of the carrier, the improvement effect of the present invention can be further enhanced. Silicone resins have an advantage of having a good spent resistance because of having a low surface energy. Any known silicone resins can be used herein. Straight silicone resins having only organosiloxane bonds, and

modified silicone resins such as alkyd-modified silicones, polyester-modified silicones, acrylic-modified silicones or urethane-modified silicones can be used for the present invention, but the silicone resin is not limited thereto.

【0050】

Specific examples of the marketed straight silicone resins include KR271, KR255 and KR152 from Shin-Etsu Chemical Co., Ltd.; and SR2400, SR2406 and SR2410 from Dow Corning Toray Silicone Co., Ltd. A straight silicone resin can be used alone or in combination with other components such as crosslinking components and/or charge control components. Specific examples of the modified silicone resins include KR206 (alkyd-modified), KR5208 (acrylic-modified), ES1001N (epoxy-modified) and KR305 (urethane-modified) from Shin-Etsu Chemical Co., Ltd.; and SR2115 (epoxy-modified) and SR2110 (alkyd-modified) from Dow Corning Toray Silicone Co., Ltd.

【0051】

Acrylic resins have high adhesion and can form a film having elasticity and good retention ability. The acrylic resins for use in the present invention mean and include all resins having an acrylic component and are not specifically limited. Acrylic resins can be used alone or in combination with one or more other components that undergo a crosslinking reaction. Suitable materials for use as the other components that undergo a crosslinking reaction include amino resins and acidic catalysts, but are not limited thereto. The amino resins include guanamine and melamine resins, but are not limited thereto. The acidic catalysts for use herein include all acidic catalysts having catalytic activity, and include acidic catalysts having a reactive group such as fully alkylated group, methylol group, imino group or methylol/imino group, but are not limited thereto.

【0052】

Thus, silicone resins and acrylic resins are used for forming a layer which is stable over a long period of time and which mainly serves to maintain satisfactory charges and resistance.

【0053】

Further, when the cover layer of the carrier includes at least a silicone resin and an acrylic resin, in which the percentage of the acrylic resin is from 10% by weight to 90% by weight, the improvement effect can be further enhanced. When the percentage falls in the range, the effects of the silicone resin and the acrylic resin can be produced while well-balanced. If the content of an acrylic resin is less than 10% by weight, the effect of the acrylic resin cannot be well produced because the content is too low. If it exceeds 90% by weight, the effect of the silicone resin cannot be well produced because the content of the acrylic resin is too high. Therefore, it is not preferable.

【0054】

In addition, it is preferable for the cover layer including a silicone resin and an acrylic resin that the silicone resin and the acrylic layer have a layered structure. In this case, the improvement effect of the present invention can be further enhanced.

【0055】

This configuration is effective to impart both of a good spent resistance function due to low surface energy of a silicone resin, and good adhesion and elasticity of an acrylic resin to a carrier. For example, when a layer of an acrylic resin is formed as a lower layer which is contacted with the surface of a core material, and a layer of a silicone resin is formed thereon as an upper layer, the carrier particles can have

a surface with good low surface energy imparted by the silicone resin, while the peeling property of the layer due to the brittleness of the silicone resin layer is remedied by the acrylic resin. However, the configuration is not limited thereto.

【0056】

Where necessary, the cover layer can further include carbon black. Carbon black significantly effectively works as a control agent for reducing the resistance of a cover layer that includes a resin alone or in combination with particles and has a high resistance. When a developer includes a carrier with high resistance, a copied image with a large image occupancy generally becomes an image with sharp "edge effect" in which the image density at a center part is very low while the image density of the edge portions is very high. By action of the edge effect, a character or thin-line image looks sharp. However, a halftone image cannot be well reproduced. When an appropriate amount of carbon black is used therefor, good images can be produced.

【0057】

Further, acrylic resins can be preferably used for a carrier for use in color developers. If a film on a carrier for color developers containing carbon black is abraded and part of the film migrates into an image, the part of the film is highly visible in the image because of having a dense color due to the carbon black, resulting in formation of a defective image. However, when the cover layer includes an acrylic resin, the acrylic resin can firmly hold carbon black in the cover layer because of having high adhesiveness and high abrasion resistance. In addition, since the acrylic resin itself has good abrasion resistance, the amount of carbon black released from the cover layer is very small. This effect can be produced

more effectively by dispersing carbon black into an acrylic resin. Any known carbon blacks, which are used for carriers and toners, can be used as the carbon black mentioned above. The carbon black is not limited thereto.

【0058】

The content of an element included in the carrier can be determined with a fluorescent X-ray analyzer ZSX 100e (available from Rigaku Corporation) using EZ scan having an element scanning function. Specifically, a sample core material or carrier is uniformly placed to a seal including a polyester film and an adhesive applied on the film. The thus prepared test sample is set on a stage, and the content is determined while setting the conditions as follows [e.g., measurement range: B-U, measurement diameter: 30 mm, sample form: metal, measurement time: long, atmosphere: vacuum] . Then the measurement is performed to determine the content of the element.

【0059】

The magnetic moment can be determined by the following method. At first, 1.0 g of a core material of a carrier is fed into a cylindrical cell. The cylindrical cell is set in a B-H Tracer type BHU-60 (available from Riken Denshi Co., Ltd.) and the sample is exposed to a varying magnetic field. Specifically, the magnetic field is gradually increased to 3000 Oe, and is then gradually decreased to zero. Thereafter, a magnetic field in an opposite direction (i.e., minus magnetic field) is applied thereto while gradually increased to -3000 Oe, and is then gradually decreased to zero. Subsequently, a magnetic field having the same direction as that of the first-mentioned magnetic field is applied again. Thus, a B-H curve is prepared. The magnetic moment at a magnetic field of 1000 Oe is determined from-the B-H curve.

【0060】

The dielectric breakdown voltage mentioned above in the paragraph (II) can be determined by the following method (see FIG. 1). A sleeve (a) is rotated at 250 rpm, and 20 g of a sample carrier (c) is placed on the rotating sleeve. Then a voltage <E> is applied between the sleeve (a) and a doctor electrode (b). Two minutes later a current <I> is read, and a resistance <R> at the applied voltage <E> is calculated according to the following equation: $R=E/I(\Omega)$. The measurement is repeated while increasing the applied voltage to detect the voltage at which a rapid drop of the resistance occurs. The dielectric breakdown voltage is defined as the applied voltage at which the rapid drop of the resistance occurs. Namely, the dielectric breakdown voltage as used herein is a voltage at which the resistance rapidly drops, i.e., an excess current rapidly flows. Namely, the dielectric breakdown voltage is defined as a voltage at which a current suddenly flows because the carrier cannot resist the voltage, although flow of current is suppressed by the carrier and only a small amount of current flows until then.

【0061】

The dielectric breakdown voltage mentioned above in paragraph (III) can be determined by the following method. At first, 200 mg of a sample carrier is placed between two electrodes set in parallel at a distance of 2 ± 0.3 mm, and magnets of 1500 Gauss are placed on the outsides of the two electrodes to form a magnetic brush of the carrier. The resistance is measured while the applied voltage is increased. The dielectric breakdown voltage is defined as the voltage at which a rapid drop of the resistance occurs. In this case, the resistance is measured using a marketed resistance measuring instrument or calculated from the applied voltage and the current measured using an ammeter.

【0062】

The weight-average particle diameter can be determined using an SRA type of Microtrac Particle Size Analyzer (available from NIKKISO Co., Ltd.). The content of particles with a particle diameter of 9 µm or less can be determined using an SRA type of Microtrac Particle Size Analyzer (available from NIKKISO Co., Ltd.) under a condition of 0.7 to 125 µm in measurement range.

【0063】

By using the developer of the present invention, which includes the carrier of the present invention and a toner containing at least a binder resin and a coloring agent, the problems of the conventional technologies can be well solved. Toners such as conventional toners prepared by kneading and pulverization and a variety of polymerization toners, which are recently used, can be used as the toner for use in the present invention.

【0064】

Suitable toners for use in the present invention will be described.

The toners preferably have a weight-average particle diameter (Dw) of 3 to 10 µm. Toners having such a weight average particle diameter can produce images with good dot reproducibility because of having a relatively small size compared to the size of fine latent image dots. If the weight-average particle diameter (Dw) is less than 3 µm, phenomena such that the toner transfer efficiency and blade-cleaning property deteriorate occur. If the weight-average particle diameter (Dw) exceeds 10 µm, it becomes difficult to prevent occurrence of scattering of character images and line images.

【0065】

The method for determining the particle size distribution of toner particles will be explained.

The particle size distribution can be determined by a method using a Coulter Counter. Specific examples thereof include a Coulter Counter Model TA-II or a Coulter Multisizer II (both available from Coulter, Inc.).

Hereinafter the measuring method will be explained.

At first, a dispersant, i.e., 0.1 ml to 5 ml of surfactant (preferably alkylbenzene sulfonate) is added to 100 ml to 150 ml of electrolytic solution. The electrolytic solution is an approximately 1% aqueous solution of first grade NaCl, and for example, ISOTON-II (available from Coulter, Inc.) can be used. Next, 2 mg to 20 mg of a test sample is added to the electrolytic solution. The electrolytic solution suspending the test sample is dispersed by an ultrasonic disperser for about 1 minute to 3 minutes. Thereafter, volume and number of the toner particles or toner are measured by the above-mentioned apparatus using an aperture of 100 μm. Then the particle diameter distributions on the volume basis and the number basis are calculated. The weight-average particle diameter (Dw) and the number-average particle diameter (Dn) are then determined from the thus determined distributions.

As channels, 13 channels of 2.00 μm to less than 2.52 μm; 2.52 μm to less than 3.17 μm; 3.17 μm to less than 4.00 μm; 4.00 μm to less than 5.04 μm; 5.04 μm to less than 6.35 μm; 6.35 μm to less than 8.00 μm; 8.00 μm to less than 10.08 μm; 10.08 μm to less than 12.70 μm; 12.70 μm to less than 16.00 μm; 16.00 μm to less than 20.20 μm; 20.20 μm to less than 25.40 μm; 25.40 μm to less than 32.00 μm; and 32.00 μm to less than 40.30 μm, are used. Namely, particles having a diameter in the range of from 2.00 μm to less than 40.30 μm are targeted.

【0066】

Known resins can be used as the binder resin of the toner for use in the present invention.

Specific examples thereof include homopolymers of styrene and substituted styrenes, such as polystyrenes, poly-p-chlorostyrene, and polyvinyl toluene; styrene copolymers such as styrene-p-chlorostyrene copolymers, styrene-propylene copolymers, styrene-vinyltoluene copolymers, styrene-methyl acrylate copolymers, styrene-ethyl acrylate copolymers, styrene-methacrylic acid copolymers, styrene-methyl methacrylate copolymers, styrene-ethyl methacrylate copolymers, styrene-butyl methacrylate copolymers, styrene-methyl (x-chloromethacrylate copolymers, styrene-acrylonitrile copolymers, styrene-vinyl methyl ether copolymers, styrene-vinyl methyl ketone copolymers, styrene-butadiene copolymers, styrene-isoprene copolymers, and styrene-maleic ester copolymers; poly(methyl methacrylate), poly(butyl methacrylate), poly(vinyl chloride), poly(vinyl acetate), polyethylenes, polyesters, polyurethanes, epoxy resins, poly(vinyl butyral), polyacrylic acid resins, rosin, modified rosin, terpene resins, phenolic resins, aliphatic or aromatic hydrocarbon resins, aromatic petroleum resins, etc. These resins can be used alone or in combination.

【0067】

Any known resins can be used as the binder resin of toner for use in image-fixation under pressure. For example, polyolefins such as low molecular weight polyethylenes, and low molecular weight polypropylenes; olefinic copolymers such as ethylene-acrylic acid copolymers, ethylene-acrylic ester copolymers, ethylene-methacrylic acid copolymers, ethylene-methacrylic ester copolymers, ethylene-vinyl chloride copolymers, ethylene-vinyl acetate copolymers, and ionomer resins; epoxy resins; polyester resins;

styrene-butadiene copolymers; polyvinylpyrrolidones; methyl vinyl ether-maleic anhydride copolymers; maleic acid-modified phenolic resins, phenol-modified terpene resins, etc. These resins can be used alone or in combination. However, the binder resin is not limited thereto.

【0068】

Any known coloring agents and pigments, which have been used for toner, can be used in the present invention. Specific examples of black coloring agents include, but are not limited to, carbon black, aniline black, furnace black, lamp black, etc.

Specific examples of cyan coloring agents include, but are not limited to, phthalocyanine blue, methylene blue, Victoria blue, methyl violet, aniline blue, ultramarine blue, etc.

Specific examples of magenta coloring agents include, but are not limited to, Rhodamine 6G lake, dimethylquinacridone, Watchung Red, rose bengal, Rhodamine 6B, alizarin lake, etc.

Specific examples of yellow coloring agents include, but are not limited to, chrome yellow, benzidine yellow, Hansa yellow, naphthol yellow, molybdate orange, quinoline yellow, tartrazine, etc.

【0069】

The toner for use in the present invention can further include a charge control agent. Specific examples of the charge control agent include known charge control agents for toner, such as nigrosine dyes, quaternary ammonium salts, amino-containing polymers, metal-containing azo dyes, salicylic acid-metal complex compounds, phenolic compounds, etc., but are not limited thereto.

【0070】

The toner for use in the present invention can further include an image-fixing aid in addition to the binder resin, coloring agent and charge control agent. By using such an aid,

the toner can also be used for an oil-less image-fixing system in which an oil for preventing toner adhesion is not applied to image-fixing rollers. Any known image-fixing aids can be used, and specific examples thereof include, but is not limited to, polyolefins such as polyethylenes, and polypropylenes; fatty acid metal salts, fatty acid esters, paraffin wax, amide waxes, polyhydric alcohol waxes, silicone varnishes, etc.

【0071】

The container of the present invention contains the developer for latent electrostatic image development of the present invention. The container has a good improvement effect such that the problems of the conventional technologies can be clearly solved.

【0072】

The image forming method of the present invention uses the developer for latent electrostatic image development of the present invention. The problems of the conventional technologies can be clearly solved by the image forming method.

FIG. 2 shows a process cartridge bearing the above-mentioned developer for latent electrostatic image development of the present invention.

FIG. 2 illustrates the entire of a process cartridge 1, and numerals 2, 3, 4 and 5 denote a photoconductor, a charging means, developing means and cleaning means, respectively.

In the process cartridge of the present invention, plural elements including the developing means 4 and at least one of the photoconductor 2, charging means 3 and cleaning means 5 are integrated. The process cartridge is detachably attached to a main body of an image forming apparatus such as copiers or printers.

【0073】

In an image forming apparatus equipped with the process

cartridge bearing the developer for latent electrostatic image development according to the present invention, the photoconductor is rotated at a predetermined peripheral speed. In the process of rotation of the photoconductor, the charging means uniformly charges the photoconductor so that a predetermined positive or negative potential is formed thereon, and then light irradiating means such as of slit irradiators or laser beam scanning irradiators, applies imagewise light to the charged photoconductor. Thus, latent electrostatic images are sequentially formed on the circumference surface of the photoconductor. The developing means develops the thus formed latent electrostatic images with toners so as to sequentially form toner images, and then the transferring means sequentially transfers the toner images onto a transfer medium which is fed from a paper feeder to a point between the photoconductor and the transfer means while synchronized with the rotation of the photoconductor. The transfer medium bearing the transferred toner images is separated from the photoconductor, and is fed to the image fixing means. The fixing means fixes the transferred image onto the transfer medium so as to form a reproduction (copy), and the copy is then discharged from the apparatus, i.e., printed out. After the toner image is transferred, cleaning means removes the toner remaining on the surface of the photoconductor to clean the surface. Thereafter, the charge of the photoconductor is eliminated such that the photoconductor is ready for another image formation.

【0074】

The process cartridge of the present invention, which bears the developer for latent electrostatic image development of the present invention, has a good improvement effect such that the problems of conventional technologies can be clearly solved. In addition, the process cartridge can be easily

attached to and detached from an image forming apparatus.

【Examples】

【0075】

Next, the present invention will be specifically explained referring to examples and comparative examples. However, the present invention is not limited thereto.

【0076】

(1) Evaluation of shape and surface conditions of a core material was performed as follows. A photograph of a sample core material before coating was taken using a field emission scanning electroscope (FE-SEM) S-4200 (available from Hitachi, Ltd.). The shape and surface conditions of the core material were rated according to the following criteria.

◎: Excellent

○: Good

△: Fair

X: Not usable in practice

The ratings ◎, ○, and △ pass, and the rating X fails the test.

(2) Evaluation of image density unevenness and roughness of half tone images was performed as follows. A halftone image was developed and outputted using a regular image forming apparatus including a two-component developing device, in which a latent electrostatic image was written by an analogue system and was developed under the following developing conditions.

- Distance between the photoconductor and developing sleeve: 0.35 mm
- Developing nip width: 3 mm
- Linear velocity of the photoconductor: 245 mm/s
- Voltage applied between the developing sleeve and photoconductor: A direct-current voltage superimposed with an alternating-current voltage with a frequency of 9 kHz and

a Vpp of 900 V

The direct-current voltage and the surface potential of the photoconductor were controlled so that the resulting halftone image has a density of about 0.8. The rate of occurrence of rough images with uneven density in the form of spot in the reproduced halftone image was graded according to the following criteria.

◎: Excellent

○: Good

△: Fair

X: Not usable in practice

The ratings ◎, ○, and △ pass, and the rating X fails the test.

(3) Evaluation of carrier adhesion was performed as follows. Development was performed while no image was formed. In this regard, background potential was controlled so as to be 150 V, and the number of carrier particles present on the photoconductor after development was counted by observation through loupe in five fields. The carrier adhesion was defined as the average number of deposited carrier particles per 100 square centimeters in the five fields and was rated according to the following criteria.

◎: Not greater than 20

○: Not less than 20 and less than 80

X: Greater than 81

The ratings ◎, and ○ pass, and the rating X fails the test.

(4) Evaluation of reproducibility of character images was performed as follows. Character images were output using a character image chart with an image occupancy of 5% (each character is about 2 mm wide and about 2 mm long), and the reproducibility of the character images was rated according to

the following criteria.

◎: Excellent

○: Good

△: Fair

X: Not usable in practice

The ratings ◎, ○, and △ pass, and the rating X fails the test.

(5) Evaluation of decrease in charge quantity after 150,000-sheet running test was performed as follows. A developer was prepared by mixing 95% by weight of a sample carrier and 5% by weight of a toner and frictionally charging the mixture. The initial charge quantity (Q1) of the developer before the running test was determined using a regular blow-off measuring instrument TB-200 (available from Toshiba Chemical Corp.). The developer was then set to a modified version of a commercially available digital full-color printer, IPSIO COLOR 8000 (available from Ricoh Company, Limited), and 150,000 copies were reproduced. Thereafter, the toner in the developer was removed using the blow-off measuring instrument, and the charge quantity (Q2) of the resulting carrier was determined using the blow-off measuring instrument to determine the charge decrease, which is obtained by subtracting Q2 from Q1. the judgment was performed such that a carrier having a charge decrease of 5.0 μc/g or less passes the test, and one having a charge decrease of exceeding 5.0 μc/g fails the test. The charge quantity is decreased due to decrease of charging sites caused by spent toner on the carrier or abrasion of the cover layer. Thus, the charge quantity decrease was used as an index for the spent toner and/or abrasion of the cover layer.

【0077】

Example 1

A carrier was prepared as follows. At first, a resinous

cover layer coating liquid was prepared by dispersing 30 parts by weight of a vinylidene fluoride-hexafluoropropylene copolymer and 100 parts by weight of dimethylformamide for 10 minutes using a HOMOMIXER mixer. The resinous cover layer coating liquid was applied to a calcined ferrite powder serving as a core material using a SPIRA COATER (available from Okada Seiko Co., Ltd.), followed by drying to form a cover layer thereon. The calcined ferrite powder had an average particle diameter of 45 μm, and a magnetic moment of 63 Am^2/kg at 1 kOe, and includes particles with a particle diameter of 9 μm or less in an amount of 0.06% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.08% by mass. The resulting carrier particles were calcined for 2 hours at 280 ℃ in an electric furnace. After cooling, the ferrite bulk was dissociated using a sieve having openings of 63 μm. Thus, Carrier 1 was prepared.

【0078】

A toner was prepared as follows. At first, in a HENSCHEL MIXER mixer rotated at 800 rpm, 100 parts by weight of a polyester resin having a softening point of 102 ℃, which serves as a binder resin, 4 parts by weight of a microwax having a melting point of 81 ℃, which serves as a wax, 2 parts by weight of a fluorine-containing quaternary ammonium salt compound, which serves as a charge control agent, and 7 parts by weight of carbon black having an average particle diameter of 50 nm, which serves as a coloring agent, were mixed. The mixture was melted and kneaded in a single-screw kneader Buss CO-KNEADER (available from Buss AG) with jacket-heating. The kneaded product was cooled and elongated using a cold-press machine, followed by rough pulverization with a cutter mill, fine pulverization with fine pulverizer using jet stream, and classification using an

air-classifier. Thus, colored mother particles having a weight-average particle diameter of 8.44 μm and a volume-average particle diameter of 7 μm were prepared.

Next, 0.5 parts by weight of a particulate colloidal silica with a degree of hydrophobicity of 50% was mixed with 100 parts by weight of the colored mother particles using a HENSCHEL MIXER mixer rotated at 700 rpm. Thus, a toner for use in evaluation of the carrier of the present invention was prepared. The weight-average particle diameter and volume-average particle diameter of the colored mother particles were determined with a Coulter Counter TA-II available from Coulter Electronics, Inc.

【0079】

The above-prepared toner was mixed with Carrier 1 in a TURBULA mixer to prepare a developer having a toner concentration of 5% by weight. The developer was placed in the modified version of a commercially available digital full-color printer IPSIO COLOR 8000 (available from Ricoh Company, Limited), and the roughness (irregularity in density) of halftone images, carrier adhesion, reproducibility of character images and decrease in charge quantity after reproduction of 150,000 copies were determined. The results are shown in Table 1.

【0080】

Example 2

The procedure for preparation of the carrier in Example 1 was repeated except that the calcined ferrite powder used as the core material was changed to a calcined ferrite powder which has an average particle diameter of 45 μm and a magnetic moment of 61 Am^2/kg at 1 kOe, and includes particles with a particle diameter of 9 μm or less in an amount of 0.05% by weight, wherein the Zr content is 0% by mass, the Bi content is 0.015% by mass,

the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.08% by mass. The thus prepared Carrier 2 was evaluated by the same method as mentioned above in Example 1. The results are shown in Table 1.

【0081】

Example 3

The procedure for preparation of the carrier in Example 1 was repeated except that the calcined ferrite powder used as the core material was changed to a calcined ferrite powder which has an average particle diameter of 45 μm and a magnetic moment of 67 Am^2/kg at 1 kOe, and includes particles with a particle diameter of 9 μm or less in an amount of 0.03% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.08% by mass. The thus prepared Carrier 3 was evaluated by the same method as mentioned above in Example 1. The results are shown in Table 1.

【0082】

Example 4

The procedure for preparation of the carrier in Example 1 was repeated except that the calcined ferrite powder used as the core material was changed to a calcined ferrite powder which has an average particle diameter of 45 μm and a magnetic moment of 75 Am^2/kg at 1 kOe, and includes particles with a particle diameter of 9 μm or less in an amount of 0.02% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.25% by mass. The thus prepared Carrier 4 was evaluated by the same method as mentioned above in Example 1. The results are shown in Table 1.

【0083】

Example 5

The procedure for preparation of the carrier in Example 1 was repeated except that the calcined ferrite powder used as the core material was changed to a calcined ferrite powder which has an average particle diameter of 19 μm and a magnetic moment of 74 Am^2/kg at 1 kOe, and includes particles with a particle diameter of 9 μm or less in an amount of 1.20% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.25% by mass, and the sieve for dissociating was replaced with a sieve with openings of 22 μm. The thus prepared Carrier 5 was evaluated by the same method as mentioned above in Example 1. The results are shown in Table 1.

【0084】

Example 6

The procedure for preparation of the carrier in Example 1 was repeated except that the calcined ferrite powder used as the core material was changed to a calcined ferrite powder which has an average particle diameter of 45 μm and a magnetic moment of 75 Am^2/kg at 1 kOe, and includes particles with a particle diameter of 9 μm or less in an amount of 3.40% by weight, wherein the Zr content is 0.14% by mass, the Bi content is 0.016% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.25% by mass. The thus prepared Carrier 6 was evaluated by the same method as mentioned above in Example 1. The results are shown in Table 1.

【0085】

Example 7

The procedure for preparation of the carrier in Example 1 was repeated except that the calcined ferrite powder used as the core material was changed to a calcined ferrite powder which has an average particle diameter of 45 μm and a magnetic moment

of 38 Am^2/kg at 1 kOe, and includes particles with a particle diameter of 9 μm or less in an amount of 0.04% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0.014% by mass, the Fe content is 41% by mass, the Mn content is 5% by mass, and the Mg content is 0.07% by mass. The thus prepared Carrier 7 was evaluated by the same method as mentioned above in Example 1. The results are shown in Table 1.

【0086】

Example 8

The procedure for preparation of the carrier in Example 1 was repeated except that the calcined ferrite powder used as the core material was changed to a calcined ferrite powder which has an average particle diameter of 45 μm and a magnetic moment of 92 Am^2/kg at 1 kOe, and includes particles with a particle diameter of 9 μm or less in an amount of 0.05% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0.015% by mass, the Fe content is 20% by mass, the Mn content is 20% by mass, and the Mg content is 0.30% by mass. The thus prepared Carrier 8 was evaluated by the same method as mentioned above in Example 1. The results are shown in Table 1.

【0087】

Example 9

The procedure for preparation of the carrier in Example 4 was repeated except that the cover resin was changed as follows.

Silicone resin solution SR2410 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 23% by weight)

132.2 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight)

0.66 parts by weight

Coloring agent: carbon black (average particle diameter of

50 nm) 7 parts by weight

Toluene 300 parts by weight

The thus prepared Carrier 9 was evaluated by the same method as mentioned above in Example 1. The results are shown in Table 1.

【0088】

Example 10

The procedure for preparation of the carrier in Example 4 was repeated except that the cover resin was changed as follows.

Acrylic resin solution (solid content of 50% by weight) 42.0 parts by weight

Guanamine solution (solid content of 70% by weight) 13.0 parts by weight

Coloring agent: carbon black (average particle diameter of 50 nm) 7 parts by weight

Toluene 60 parts by weight

Butylcellosolve 60 parts by weight

The thus prepared Carrier 10 was evaluated by the same method as mentioned above in Example 1. The results are shown in Table 1.

【0089】

Example 11

The procedure for preparation of the carrier in Example 4 was repeated except that the cover resin was changed as follows.

Silicone resin solution SR2410 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 23% by weight) 66.1 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight) 0.33 parts by weight

Acrylic resin solution (solid content of 50% by weight)
21.0 parts by weight

Guanamine solution (solid content of 70% by weight)
6.5 parts by weight

Coloring agent: carbon black (average particle diameter of 50 nm) 7 parts by weight

Toluene 180 parts by weight

Butylcellosolve 30 parts by weight

The thus prepared Carrier 11 was evaluated by the same method as mentioned above in Example 1. The results are shown in Table 1.

【0090】

Example 12

The procedure for preparation of the carrier in Example 11 was repeated except that the calcined ferrite powder used as the core material was changed to a calcined ferrite powder which has an average particle diameter of 35 μm and a magnetic moment of 74 Am^2/kg at 1 kOe, and includes particles with a particle diameter of 9 μm or less in an amount of 0.01% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.25% by mass; and the cover resin was changed as follows.

Silicone resin solution SR2410 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 23% by weight)
85.0 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight)
0.42 parts by weight

Acrylic resin solution (solid content of 50% by weight)
27.0 parts by weight

Guanamine solution (solid content of 70% by weight)

8.4 parts by weight

Coloring agent: carbon black (average particle diameter of 50 nm) 9 parts by weight

Toluene 230 parts by weight

Butylcellosolve 40 parts by weight

The thus prepared Carrier 12 was evaluated by the same method as mentioned above in Example 1. The results are shown in Table 1.

【0091】

Example 13

The procedure for preparation of the carrier in Example 4 was repeated except that the cover resin was changed as follows.

Silicone resin solution SR2410 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 23% by weight) 123.9 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight) 0.33 parts by weight

Acrylic resin solution (solid content of 50% by weight) 3.0 parts by weight

Guanamine solution (solid content of 70% by weight) 0.65 parts by weight

Coloring agent: carbon black (average particle diameter of 50 nm) 7 parts by weight

Toluene 180 parts by weight

Butylcellosolve 30 parts by weight

The thus prepared Carrier 13 was evaluated by the same method as mentioned above in Example 1. The results are shown in Table 1.

【0092】

Example 14

The procedure for preparation of the carrier in Example 4 was repeated except that the cover resin was changed as follows.

Silicone resin solution SR2410 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 23% by weight)
6.5 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight)
0.33 parts by weight

Acrylic resin solution (solid content of 50% by weight)
57.0 parts by weight

Guanamine solution (solid content of 70% by weight)
12.4 parts by weight

Coloring agent: carbon black (average particle diameter of 50 nm) 7 parts by weight

Toluene 80 parts by weight

Butylcellosolve 30 parts by weight

The thus prepared Carrier 14 was evaluated by the same method as mentioned above in Example 1. The results are shown in Table 1.

【0093】

Example 15

A resinous cover layer coating liquid for preparing a lower layer was prepared in the same manner explained in Example 4. Namely, the following components were dispersed for 10 minutes using a HOMOMIXER mixer.

Acrylic resin solution (solid content of 50% by weight)
21.0 parts by weight

Guanamine solution (solid content of 70% by weight)
6.5 parts by weight

Coloring agent: carbon black (average particle diameter of 50 nm) 7 parts by weight

Toluene 30 parts by weight

Butylcellosolve 30 parts by weight

The resinous cover layer coating liquid was applied to the same core material as used in Example 4, using a SPIRA COATER (available from Okada Seiko Co., Ltd.), followed by drying to form an intermediate carrier having a lower cover layer thereon.

【0094】

Then a resinous cover layer coating liquid for preparing an upper layer was prepared. Namely, the following components were dispersed for 10 minutes using a HOMOMIXER mixer.

Silicone resin solution SR2410 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 23% by weight) 66.1 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight) 0.33 parts by weight

Toluene 150 parts by weight

The resinous cover layer coating liquid was applied to the above-prepared intermediate carrier, followed by drying to form an upper cover layer thereon. The resulting carrier particles were calcined for 1 hour at 180 ℃ in an electric furnace. After cooling, the ferrite bulk was dissociated using a sieve having openings of 63 μm. Thus, Carrier 15 was prepared. The thus prepared Carrier 15 was evaluated by the same method as mentioned above in Example 1. The results are shown in Table 1.

【0095】

Comparative Example 1

The procedure for preparation of the carrier in Example 1 was repeated except that the calcined ferrite powder used as the core material was changed to a calcined ferrite powder which has an average particle diameter of 45 μm, and a magnetic moment

of 65 Am^2/kg at 1 kOe, and includes particles with a particle diameter of 9 µm or less in an amount of 0.06% by weight, wherein the Zr content is 0% by mass, the Bi content is 0% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.08% by mass. The thus prepared Carrier 16 was evaluated by the same method as mentioned above in Example 1. The results are shown in Table 1.

【0096】

Comparative Example 2

The procedure for preparation of the carrier in Example 1 was repeated except that the calcined ferrite powder used as the core material was changed to a calcined ferrite powder which has an average particle diameter of 45 µm and a magnetic moment of 58 Am^2/kg at 1 kOe, and includes particles with a particle diameter of 9 µm or less in an amount of 0.05% by weight, wherein the Zr content is 8% by mass, the Bi content is 0% by mass, the Fe content is 12% by mass, the Mn content is 25% by mass, and the Mg content is 0.08% by mass. The thus prepared Carrier 17 was evaluated by the same method as mentioned above in Example 1. The results are shown in Table 1.

【0097】

Comparative Example 3

The procedure for preparation of the carrier in Example 1 was repeated except that the calcined ferrite powder used as the core material was changed to a calcined ferrite powder which has an average particle diameter of 45 µm and a magnetic moment of 57 Am^2/kg at 1 kOe, and includes particles with a particle diameter of 9 µm or less in an amount of 0.05% by weight, wherein the Zr content is 0% by mass, the Bi content is 3% by mass, the Fe content is 13% by mass, the Mn content is 25% by mass, and the Mg content is 0.08% by mass. The thus prepared Carrier 18 was evaluated by the same method as mentioned above in Example

1. The results are shown in Table 1.

【0098】

【Table 1】

	Image density unevenness in half tone image	Carrier Adhesion	Reproducibility of character images	Decrease in charge quantity after running test (μc/g)
Ex. 1	○	◎	◎	4.2
Ex. 2	○	◎	◎	4.3
Ex. 3	○	◎	◎	4.0
Ex. 4	○	◎	◎	4.1
Ex. 5	○	○	◎	4.2
Ex. 6	○	○	◎	4.1
Ex. 7	○	○	◎	4.7
Ex. 8	○	◎	○	4.8
Ex. 9	○	◎	◎	2.6
Ex. 10	○	◎	◎	3.0
Ex. 11	○	◎	◎	1.9
Ex. 12	○	◎	◎	2.3
Ex. 13	○	◎	◎	2.7
Ex. 14	○	◎	◎	2.9
Ex. 15	○	◎	◎	1.2
Comp. Ex. 1	X	Not evaluated due to serious image density unevenness of half tone images.		
Comp. Ex. 2	X	Not evaluated due to serious image density unevenness of half tone images.		

Comp. Ex. 3	X	Not evaluated due to serious image density unevenness of half tone images.

【0099】

Carriers 1 to 15 passed the test with all the properties evaluated, namely they obtained good results.

Since the half tone images produced by Carriers 16 to 18 had uneven density (irregular densities) such that the carriers are not usable in practice, the carriers were considered to fail the test, and the other evaluations were not performed.

【0100】

Example 16

A carrier was prepared as follows. At first, a resinous cover layer coating liquid was prepared by dispersing 30 parts by weight of a vinylidene fluoride-hexafluoropropylene copolymer and 100 parts by weight of dimethylformamide for 10 minutes using a HOMOMIXER mixer. The resinous cover layer coating liquid was applied to a calcined ferrite powder, which serves as a core material and which includes Fe, Mn, Mg and Zr as main elements, using a SPIRA COATER (available from Okada Seiko Co., Ltd.), followed by drying to form a cover layer thereon. The thus prepared carrier was calcined for 2 hours at 280 ℃ in an electric furnace. After cooling, the ferrite bulk was dissociated using a sieve having openings of 63 μm. Thus, Carrier 19 was prepared. The thus prepared carrier has an average particle diameter of 45 μm and a magnetic moment of 63 Am^2/kg at 1 kOe, and includes particles with a particle diameter of 9 μm or less in an amount of 0.05% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0% by mass, the Fe content is 25% by mass, the Mn content is 14% by mass, and the Mg content is 0.07% by mass.

【0101】

A toner was prepared as follows. At first, in a HENSCHEL MIXER mixer rotated at 800 rpm, 100 parts by weight of a polyester resin having a softening point of 102 ℃, which serves as a binder resin, 4 parts by weight of a microwax having a melting point of 81 ℃, which serves as a wax, 2 parts by weight of a fluorine-containing quaternary ammonium salt compound, which serves as a charge control agent, and 7 parts by weight of carbon black having an average particle diameter of 50 nm, which serves as a coloring agent, were mixed. The mixture was melted and kneaded in a single-screw kneader Buss CO-KNEADER (available from Buss AG), which was heated to 120 ℃ with jacket-heating. The kneaded product was cooled and elongated using a cold-press machine, followed by rough pulverization with a cutter mill, fine pulverization with fine pulverizer using jet stream, and classification using an air-classifier. Thus, colored mother particles having a weight-average particle diameter of 8.42 μm and a volume-average particle diameter of 7 μm were prepared.

Next, 0.5 parts by weight of a particulate colloidal silica with a degree of hydrophobicity of 50% was mixed with 100 parts by weight of the colored mother particles using a HENSCHEL MIXER mixer rotated at 700 rpm. Thus, a toner for use in evaluation of the carrier of the present invention was prepared. The weight-average particle diameter and volume-average particle diameter of the colored mother particles were determined with a Coulter Counter TA-II available from Coulter Electronics, Inc.

【0102】

The above-prepared toner was mixed with Carrier 19 in a TURBULA mixer to prepare a developer having a toner concentration of 5% by weight. The developer was placed in the modified version of a commercially available digital full-color printer IPSIO COLOR 8000 (available from Ricoh Company,

Limited), and the roughness (irregularity in density) of halftone images, carrier adhesion, reproducibility of character images and decrease in charge quantity after reproduction of 150,000 copies were determined. The results are shown in Table 2.

【0103】

Example 17

The procedure for preparation of the carrier in Example 16 was repeated except that the calcined ferrite powder used as the core material was changed to a calcined ferrite powder which has an average particle diameter of 45 μm, and includes Fe, Mn, Mg and Bi as main elements. The thus prepared carrier had an average particle diameter of 45 μm a magnetic moment of 60 Am^2/kg at 1 kOe, and includes particles with a particle diameter of 9 μm or less in an amount of 0.05% by weight, wherein the Zr content is 0% by mass, the Bi content is 0.016% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.06% by mass. The thus prepared Carrier 20 was evaluated by the same method as mentioned above in Example 16. The results are shown in Table 2.

【0104】

Example 18

The procedure for preparation of the carrier in Example 16 was repeated except that the calcined ferrite powder used as the core material was changed to a calcined ferrite powder which has an average particle diameter of 45 μm, and includes Fe, Mn, Mg, Zr and Bi as main elements. The thus prepared carrier had an average particle diameter of 45 μm a magnetic moment of 67 Am^2/kg at 1 kOe, and includes particles with a particle diameter of 9 μm or less in an amount of 0.02% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass, the Mn content is 13%

by mass, and the Mg content is 0.06% by mass. The thus prepared Carrier 21 was evaluated by the same method as mentioned above in Example 16. The results are shown in Table 2.

【0105】

Example 19

The procedure for preparation of the carrier in Example 16 was repeated except that the calcined ferrite powder used as the core material was changed to a calcined ferrite powder which includes a relatively large amount of Mg. The thus prepared carrier had an average particle diameter of 45 μm, a magnetic moment of 76 Am^2/kg at 1 kOe, and included particles with a particle diameter of 9 μm or less in an amount of 0.03% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0.016% by mass, the Fe content is 25% by mass, the Mn content is 14% by mass, and the Mg content is 0.20% by mass. The thus prepared Carrier 22 was evaluated by the same method as mentioned above in Example 16. The results are shown in Table 2.

【0106】

Example 20

The procedure for preparation of the carrier in Example 16 was repeated except that the average particle diameter of the calcined ferrite powder used as the core material was changed to 19 μm and the sieve was replaced with a sieve having openings of 22 μm. The thus prepared carrier had an average particle diameter of 19 μm a magnetic moment of 75 Am^2/kg at 1 kOe, and included particles with a particle diameter of 9 μm or less in an amount of 1.30% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0.016% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.19% by mass. The thus prepared Carrier 23 was evaluated by the same method as mentioned above in Example 16. The results

are shown in Table 2.

【0107】

Example 21

The procedure for preparation of the carrier in Example 16 was repeated except that the calcined ferrite powder used as the core material was replaced with one including fine particles at a high content. The thus prepared carrier had an average particle diameter of 45 μm, and a magnetic moment of 75 Am^2/kg at 1 kOe, and included particles with a particle diameter of 9 μm or less in an amount of 3.30% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0.016% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.19% by mass. The thus prepared Carrier 24 was evaluated by the same method as mentioned above in Example 16. The results are shown in Table 2.

【0108】

Example 22

The procedure for preparation of the carrier in Example 16 was repeated except that the calcined ferrite powder used as the core material was replaced with one in which the ratio of the constitutional elements is changed to decrease the magnetic moment. The thus prepared carrier had an average particle diameter of 45 μm and a magnetic moment of 37 Am^2/kg at 1 kOe, and included particles with a particle diameter of 9 μm or less in an amount of 0.05% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0.016% by mass, the Fe content is 39% by mass, the Mn content is 5% by mass, and the Mg content is 0.08% by mass. The thus prepared Carrier 25 was evaluated by the same method as mentioned above in Example 16. The results are shown in Table 2.

【0109】

Example 23

The procedure for preparation of the carrier in Example 16 was repeated except that the calcined ferrite powder used as the core material was replaced with one in which the ratio of the constitutional elements is changed to increase the magnetic moment. The thus prepared carrier had an average particle diameter of 45 μm and a magnetic moment of 93 Am^2/kg at 1 kOe, and included particles with a particle diameter of 9 μm or less in an amount of 0.04% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0.015% by mass, the Fe content is 21% by mass, the Mn content is 19% by mass, and the Mg content is 0.26% by mass. The thus prepared Carrier 26 was evaluated by the same method as mentioned above in Example 16. The results are shown in Table 2.

【0110】

Example 24

The procedure for preparation of the carrier in Example 19 was repeated except that the cover resin was changed as follows.

Silicone resin solution SR2410 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 23% by weight) 132.2 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight) 0.66 parts by weight

Carbon black serving as coloring agent (particle diameter of 50 nm) 7 parts by weight

Toluene 300 parts by weight

The thus prepared carrier had an average particle diameter of 45 μm and a magnetic moment of 76 Am^2/kg at 1 kOe, and included particles with a particle diameter of 9 μm or less in an amount of 0.03% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass,

the Mn content is 13% by mass, and the Mg content is 0.20% by mass. The thus prepared Carrier 27 was evaluated by the same method as mentioned above in Example 16. The results are shown in Table 2.

【0111】

Example 25

The procedure for preparation of the carrier in Example 19 was repeated except that the cover resin was changed as follows.

Acrylic resin (solid content: 50% by weight) 42.0 parts by weight

Guanamine solution (solid content: 70% by weight) 13.0 parts by weight

Carbon black serving as coloring agent (particle diameter of 50 nm) 7 parts by weight

Toluene 60 parts by weight

Butylcellosolve 60 parts by weight

The thus prepared carrier had an average particle diameter of 45 μm and a magnetic moment of 75 Am^2/kg at 1 kOe, and included particles with a particle diameter of 9 μm or less in an amount of 0.02% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass, the Mn content is 14% by mass, and the Mg content is 0.19% by mass. The thus prepared Carrier 28 was evaluated by the same method as mentioned above in Example 16. The results are shown in Table 2.

【0112】

Example 26

The procedure for preparation of the carrier in Example 19 was repeated except that the cover resin was changed as follows.

Silicone resin solution SR2410 (available from Dow Corning

Toray Silicone Co., Ltd.; solid content: 23% by weight)
66.1 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight)
0.33 parts by weight

Acrylic resin (solid content: 50% by weight)
21.0 parts by weight

Guanamine solution (solid content: 70% by weight)
6.5 parts by weight

Carbon black serving as coloring agent (particle diameter of 50 nm) 7 parts by weight

Toluene 180 parts by weight

Butylcellosolve 30 parts by weight

The thus prepared carrier had an average particle diameter of 45 μm and a magnetic moment of 76 Am^2/kg at 1 kOe, and included particles with a particle diameter of 9 μm or less in an amount of 0.03% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0.016% by mass, the Fe content is 25% by mass, the Mn content is 14% by mass, and the Mg content is 0.19% by mass. The thus prepared Carrier 29 was evaluated by the same method as mentioned above in Example 16. The results are shown in Table 2.

【0113】

Example 27

The procedure for preparation of the carrier in Example 26 was repeated except that the calcined ferrite powder used as the core material was replaced with a calcined ferrite powder having a small particle diameter, and the cover resin was changed as follows.

Silicone resin solution SR2410 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 23% by weight)
85.0 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight)

0.42 parts by weight

Acrylic resin (solid content: 50% by weight)

27.0 parts by weight

Guanamine solution (solid content: 70% by weight)

8.4 parts by weight

Carbon black serving as coloring agent (particle diameter of 50 nm) 9 parts by weight

Toluene 230 parts by weight

Butylcellosolve 40 parts by weight

The thus prepared carrier had an average particle diameter of 35 μm and a magnetic moment of 75 Am^2/kg at 1 kOe, and included particles with a particle diameter of 9 μm or less in an amount of 0.11% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass, the Mn content is 14% by mass, and the Mg content is 0.20% by mass. The thus prepared Carrier 30 was evaluated by the same method as mentioned above in Example 16. The results are shown in Table 2.

【0114】

Example 28

The procedure for preparation of the carrier in Example 19 was repeated except that the cover resin was changed as follows.

Silicone resin solution SR2410 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 23% by weight)

123.9 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight)

0.33 parts by weight

Acrylic resin (solid content: 50% by weight)

3.0 parts by weight

Guanamine solution (solid content: 70% by weight)

0.65 parts by weight

Carbon black serving as coloring agent (particle diameter of 50 nm) 7 parts by weight

Toluene 180 parts by weight

Butylcellosolve 30 parts by weight

The thus prepared carrier had an average particle diameter of 45 μm and a magnetic moment of 75 Am^2/kg at 1 kOe, and included particles with a particle diameter of 9 μm or less in an amount of 0.03% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.19% by mass. The thus prepared Carrier 31 was evaluated by the same method as mentioned above in Example 16. The results are shown in Table 2.

【0115】

Example 29

The procedure for preparation of the carrier in Example 19 was repeated except that the cover resin was changed as follows.

Silicone resin solution SR2410 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 23% by weight)

6.5 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight)

0.33 parts by weight

Acrylic resin (solid content: 50% by weight)

57.0 parts by weight

Guanamine solution (solid content: 70% by weight)

12.4 parts by weight

Carbon black serving as coloring agent (particle diameter

of 50 nm) 7 parts by weight

Toluene 80 parts by weight

Butylcellosolve 30 parts by weight

The thus prepared carrier had an average particle diameter of 45 μm and a magnetic moment of 76 Am^2/kg at 1 kOe, and included particles with a particle diameter of 9 μm or less in an amount of 0.02% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0.016% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.20% by mass. The thus prepared Carrier 32 was evaluated by the same method as mentioned above in Example 16. The results are shown in Table 2.

【0116】

Example 30

A resinous cover layer coating liquid for preparing a lower layer was prepared in the same manner explained in Example 19. Namely, the following components were dispersed for 10 minutes using a HOMOMIXER mixer.

Acrylic resin solution (solid content of 50% by weight) 21.0 parts by weight

Guanamine solution (solid content of 70% by weight) 6.5 parts by weight

Coloring agent: carbon black (average particle diameter of 50 nm) 7 parts by weight

Toluene 30 parts by weight

Butylcellosolve 30 parts by weight

The resinous cover layer coating liquid was applied to the same core material as used in Example 19, using a SPIRA COATER (available from Okada Seiko Co., Ltd.), followed by drying to form an intermediate carrier having a lower cover layer thereon.

【0117】

Then a resinous cover layer coating liquid for preparing

an upper layer was prepared. Namely, the following components were dispersed for 10 minutes using a HOMOMIXER mixer.

Silicone resin solution SR2410 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 23% by weight)
66.1 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight)
0.33 parts by weight

Toluene 150 parts by weight

The resinous cover layer coating liquid was applied to the above-prepared intermediate carrier, followed by drying to form an upper cover layer thereon. The resulting carrier particles were calcined for 1 hour at 180 ℃ in an electric furnace. After cooling, the ferrite bulk was dissociated using a sieve having openings of 63 μm. Thus, a Carrier 33 was prepared. The thus prepared carrier had an average particle diameter of 45 μm and a magnetic moment of 76 Am^2/kg at 1 kOe, and included particles with a particle diameter of 9 μm or less in an amount of 0.02% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.20% by mass. The thus prepared Carrier 33 was evaluated by the same method as mentioned above in Example 16. The results are shown in Table 2.

【0118】

Comparative Example 4

The procedure for preparation of the carrier in Example 16 was repeated except that the calcined ferrite powder used as the core material was replaced with one which does not include Zr. The thus prepared carrier had an average particle diameter of 45 μm and a magnetic moment of 64 Am^2/kg at 1 kOe, and included particles with a particle diameter of 9 μm or less in an amount

of 0.05% by weight, wherein the Zr content is 0% by mass, the Bi content is 0% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.08% by mass. The thus prepared Carrier 34 was evaluated by the same method as mentioned above in Example 16. The results are shown in Table 2.

【0119】

Comparative Example 5

The procedure for preparation of the carrier in Example 16 was repeated except that the calcined ferrite powder used as the core material was replaced with one including a relatively large amount of Zr. The thus prepared carrier had an average particle diameter of 45 μm and a magnetic moment of 57 Am^2/kg at 1 kOe, and included particles with a particle diameter of 9 μm or less in an amount of 0.06% by weight, wherein the Zr content is 7% by mass, the Bi content is 0% by mass, the Fe content is 9% by mass, the Mn content is 24% by mass, and the Mg content is 0.07% by mass. The thus prepared Carrier 35 was evaluated by the same method as mentioned above in Example 16. The results are shown in Table 2.

【0120】

Comparative Example 6

The procedure for preparation of the carrier in Example 17 was repeated except that the calcined ferrite powder used as the core material was replaced with one including a relatively large amount of Bi. The thus prepared carrier had an average particle diameter of 45 μm and a magnetic moment of 56 Am^2/kg at 1 kOe, and included particles with a particle diameter of 9 μm or less in an amount of 0.05% by weight, wherein the Zr content is 0% by mass, the Bi content is 3% by mass, the Fe content is 9% by mass, the Mn content is 25% by mass, and the Mg content is 0.08% by mass. The thus prepared Carrier 36

was evaluated by the same method as mentioned above in Example 16. The results are shown in Table 2.

【0121】

【Table 2】

	Shape and surface conditions of core material	Image density unevenness in half tone image	Carrier Adhesion	Reproducibility of character images	Decrease in charge quantity after running test (μc/g)
Ex. 16	○	○	◎	◎	4.3
Ex. 17	◎	○	◎	◎	4.1
Ex. 18	◎	◎	◎	◎	4.2
Ex. 19	◎	◎	◎	◎	4.0
Ex. 20	◎	◎	○	◎	4.4
Ex. 21	◎	◎	○	◎	4.1
Ex. 22	◎	○	○	◎	4.7
Ex. 23	◎	○	◎	○	4.9
Ex. 24	◎	◎	◎	◎	2.5
Ex. 25	◎	◎	◎	◎	3.1
Ex. 26	◎	◎	◎	◎	1.8
Ex. 27	◎	◎	◎	◎	2.0
Ex. 28	◎	◎	◎	◎	2.6
Ex. 29	◎	◎	◎	◎	3.0
Ex. 30	◎	◎	◎	◎	1.1
Comp. Ex. 4	○	X	Not evaluated.		
Comp. Ex. 5	△	X	X	Not evaluated.	

Comp. Ex. 6	△	X	X	Not evaluated.

【0122】

Carriers 19 to 33 passed with respect to all the properties evaluated, namely they obtained good results.

Since the half tone images produced by Carrier 34 had uneven density such that the carrier is not usable in practice, the carrier was considered to fail the test, and the other evaluations were not performed.

Since the half tone images produced by Carriers 35 and 36 had uneven density such that the carriers are not usable in practice and caused carrier adhesion, the carriers were considered to fail the test, and the other evaluations were not performed.

【0123】

Example 31

A carrier was prepared as follows. At first, a resinous cover layer coating liquid was prepared by dispersing 30 parts by weight of a vinylidene fluoride-hexafluoropropylene copolymer and 100 parts by weight of dimethylformamide for 10 minutes using a HOMOMIXER mixer. The resinous cover layer coating liquid was applied to a calcined ferrite powder, which serves as a core material and which includes Fe, Mn, Mg and Zr as main elements, using a SPIRA COATER (available from Okada Seiko Co., Ltd.), followed by drying to form a cover layer thereon. The thus prepared carrier was calcined for 2 hours at 280 ℃ in an electric furnace. After cooling, the ferrite bulk was dissociated using a sieve having openings of 63 μm. Thus, Carrier 37 was prepared. The thus prepared carrier had an average particle diameter of 45 μm, a magnetic moment of 66 Am^2/kg at 1 kOe, and a dielectric breakdown voltage of 1100 V, and included particles with a particle diameter of 9 μm or less

in an amount of 0.07% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.06% by mass. The dielectric breakdown voltage was measured with an instrument which includes a rotation sleeve having a fixed magnet therein and an electrode set 1 mm apart from the sleeve and which applies a DC voltage.

【0124】

A toner was prepared as follows. At first, in a HENSCHEL MIXER mixer rotated at 800 rpm, 100 parts by weight of a polyester resin having a softening point of 102 ℃, which serves as a binder resin, 4 parts by weight of a microwax having a melting point of 81 ℃, which serves as a wax, 2 parts by weight of a fluorine-containing quaternary ammonium salt compound, which serves as a charge control agent, and 7 parts by weight of carbon black having an average particle diameter of 50 nm, which serves as a coloring agent, were mixed. The mixture was melted and kneaded in a single-screw kneader Buss CO-KNEADER (available from Buss AG), which was heated to 120 ℃ with jacket-heating. The kneaded product was cooled and elongated using a cold-press machine, followed by rough pulverization with a cutter mill, fine pulverization with fine pulverizer using jet stream, and classification using an air-classifier. Thus, colored mother particles having a weight-average particle diameter of 8.40 μm and a volume-average particle diameter of 7 μm were prepared.

Next, 0.5 parts by weight of a particulate colloidal silica with a degree of hydrophobicity of 50% was mixed with 100 parts by weight of the colored mother particles using a HENSCHEL MIXER mixer rotated at 700 rpm. Thus, a toner for use in evaluation of the carrier of the present invention was prepared. The weight-average particle diameter and volume-average particle diameter of the colored mother particles were determined with

a Coulter Counter TA-II available from Coulter Electronics, Inc.

【0125】

The above-prepared toner was mixed with Carrier 37 in a TURBULA mixer to prepare a developer having a toner concentration of 5% by weight. The developer was placed in the modified version of a commercially available digital full-color printer IPSIO COLOR 8000 (available from Ricoh Company, Limited), and the roughness (irregularity in density) of halftone image, carrier adhesion, reproducibility of character image and decrease in charge quantity after reproduction of 150,000 copies were determined. The results are shown in Table 3.

【0126】

Example 32

The procedure for preparation of the carrier in Example 31 was repeated except that the calcined ferrite powder used as the core material was changed to a calcined ferrite powder which has an average particle diameter of 45 μm, and includes Fe, Mn, Mg and Bi as main elements. The thus prepared carrier had an average particle diameter of 45 μm, a magnetic moment of 65 Am^2/kg at 1 kOe, and a dielectric breakdown voltage of 1200 V, and included particles with a particle diameter of 9 μm or less in an amount of 0.06% by weight, wherein the Zr content is 0% by mass, the Bi content is 0.016% by mass, the Fe content is 25% by mass, the Mn content is 14% by mass, and the Mg content is 0.07% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 31. The thus prepared Carrier 38 was evaluated by the same method as mentioned above in Example 31. The results are shown in Table 3.

【0127】

Example 33

The procedure for preparation of the carrier in Example 31 was repeated except that the calcined ferrite powder used as the core material was changed to a calcined ferrite powder which has an average particle diameter of 45 μm, and includes Fe, Mn, Mg, Zr and Bi as main elements. The thus prepared carrier had an average particle diameter of 45 μm, a magnetic moment of 68 Am^2/kg at 1 kOe, and a dielectric breakdown voltage of 1600 V, and included particles with a particle diameter of 9 μm or less in an amount of 0.05% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.06% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 31. The thus prepared Carrier 39 was evaluated by the same method as mentioned above in Example 31. The results are shown in Table 3.

【0128】

Example 34

The procedure for preparation of the carrier in Example 33 was repeated except that the calcined ferrite powder used as the core material was changed to a calcined ferrite powder which includes a relatively large amount of Mg. The thus prepared carrier had an average particle diameter of 45 μm, a magnetic moment of 75 Am^2/kg at 1 kOe, and a dielectric breakdown voltage of 2000 V, and included particles with a particle diameter of 9 μm or less in an amount of 0.03% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.21% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 31. The thus prepared Carrier 40 was evaluated

by the same method as mentioned above in Example 31. The results are shown in Table 3.

【0129】

Example 35

The procedure for preparation of the carrier in Example 34 was repeated except that the calcined ferrite powder used as the core material was replaced with a calcined ferrite powder having a small average particle diameter of 19 µm and the sieve was replaced with a sieve having openings of 22 µm. In addition, the cover resin was changed as follows.

Vinylidene fluoride-hexafluoropropylene copolymer	71 parts by weight
Dimethylformamide	237 parts by weight

The thus prepared carrier had an average particle diameter of 19 µm, a magnetic moment of 76 Am^2/kg at 1 kOe and a dielectric breakdown voltage of 2000 V, and included particles with a particle diameter of 9 µm or less in an amount of 1.33% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0.016% by mass, the Fe content is 25% by mass, the Mn content is 14% by mass, and the Mg content is 0.20% by mass. The dielectric breakdown voltage was measured in the same manner described in Example 31. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 31. The thus prepared Carrier 41 was evaluated by the same method as mentioned above in Example 31. The results are shown in Table 3.

【0130】

Example 36

The procedure for preparation of the carrier in Example 35 was repeated except that the calcined ferrite powder used as the core material was replaced with a calcined ferrite powder having a large average particle diameter of 70 µm and the sieve

was replaced with a sieve having openings of 106 μm. In addition, the cover resin was changed as follows.

Vinylidene fluoride-hexafluoropropylene copolymer
20 parts by weight

Dimethylformamide 65 parts by weight

The thus prepared carrier had an average particle diameter of 70 μm, a magnetic moment of 73 Am^2/kg at 1 kOe and a dielectric breakdown voltage of 2100 V, and included particles with a particle diameter of 9 μm or less in an amount of 0.01% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.19% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 31. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 31. The thus prepared Carrier 42 was evaluated in the same manner explained in Example 31. The results are shown in Table 3.

【0131】

Example 37

The procedure for preparation of the carrier in Example 34 was repeated except that the calcined ferrite powder used as the core material was replaced with one including fine particles at a high content. The thus prepared carrier had an average particle diameter of 45 μm, a magnetic moment of 76 Am^2/kg at 1 kOe and a dielectric breakdown voltage of 1800 V, and included particles with a particle diameter of 9 μm or less in an amount of 3.35% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0.016% by mass, the Fe content is 25% by mass, the Mn content is 14% by mass, and the Mg content is 0.20% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 31. The thus

prepared Carrier 43 was evaluated by the same method as mentioned above in Example 31. The results are shown in Table 3.

【0132】

Example 38

The procedure for preparation of the carrier in Example 34 was repeated except that the calcining temperature was changed to 300 ℃, and the cover resin was changed as follows.

Silicone resin solution SR2410 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 23% by weight) 132.2 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight) 0.66 parts by weight

Carbon black serving as coloring agent (particle diameter of 50 nm) 7 parts by weight

Toluene 300 parts by weight

The thus prepared carrier had an average particle diameter of 45 μm, a magnetic moment of 76 Am^2/kg at 1 kOe and a dielectric breakdown voltage of 2100 V, and included particles with a particle diameter of 9 μm or less in an amount of 0.02% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.21% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 31. The thus prepared Carrier 44 was evaluated by the same method as mentioned above in Example 31. The results are shown in Table 3.

【0133】

Example 39

The procedure for preparation of the carrier in Example 34 was repeated except that the calcining temperature was

changed to 150 ℃ and the cover resin was changed as follows.

Acrylic resin (solid content: 50% by weight)
42.0 parts by weight

Guanamine solution (solid content: 70% by weight)
13.0 parts by weight

Carbon black serving as coloring agent (particle diameter of 50 nm) 7 parts by weight

Toluene 60 parts by weight

Butylcellosolve 60 parts by weight

The thus prepared carrier had an average particle diameter of 45 μm, a magnetic moment of 75 Am^2/kg at 1 kOe and a dielectric breakdown voltage of 2200 V, and included particles with a particle diameter of 9 μm or less in an amount of 0.03% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass, the Mn content is 14% by mass, and the Mg content is 0.19% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 31. The thus prepared Carrier 45 was evaluated by the same method as mentioned above in Example 31. The results are shown in Table 3.

【0134】

Example 40

The procedure for preparation of the carrier in Example 34 was repeated except that the calcining temperature was changed to 150 ℃ and the cover resin was changed as follows.

Silicone resin solution SR2410 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 23% by weight)
66.1 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight)
0.33 parts by weight

Acrylic resin (solid content: 50% by weight)

21.0 parts by weight

Guanamine solution (solid content: 70% by weight)

6.5 parts by weight

Carbon black serving as coloring agent (particle diameter of 50 nm) 7 parts by weight

Toluene 180 parts by weight

Butylcellosolve 30 parts by weight

The thus prepared carrier had an average particle diameter of 45 μm, a magnetic moment of 76 Am^2/kg at 1 kOe, and a dielectric breakdown voltage of 2200 V, and included particles with a particle diameter of 9 μm or less in an amount of 0.02% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0.016% by mass, the Fe content is 25% by mass, the Mn content is 14% by mass, and the Mg content is 0.21% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 31. The thus prepared Carrier 46 was evaluated by the same method as mentioned above in Example 31. The results are shown in Table 3.

【0135】

Example 41

The procedure for preparation of the carrier in Example 40 was repeated except that the calcined ferrite powder used as the core material was replaced with a calcined ferrite powder having a small particle diameter of 35 μm, and the cover resin was changed as follows.

Silicone resin solution SR2410 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 23% by weight)

85.0 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight)

0.42 parts by weight

Acrylic resin (solid content: 50% by weight)

27.0 parts by weight

Guanamine solution (solid content: 70% by weight)

8.4 parts by weight

Carbon black serving as coloring agent (particle diameter of 50 nm) 9 parts by weight

Toluene 230 parts by weight

Butylcellosolve 40 parts by weight

The thus prepared carrier had an average particle diameter of 35 μm, a magnetic moment of 76 Am^2/kg at 1 kOe and a dielectric breakdown voltage of 2300 V, and included particles with a particle diameter of 9 μm or less in an amount of 0.12% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0.016% by mass, the Fe content is 25% by mass, the Mn content is 14% by mass, and the Mg content is 0.20% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 31. The thus prepared Carrier 47 was evaluated by the same method as mentioned above in Example 31. The results are shown in Table 3.

【0136】

Example 42

The procedure for preparation of the carrier in Example 40 was repeated except that the cover resin was changed as follows.

Silicone resin solution SR2410 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 23% by weight)

123.9 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight)

0.33 parts by weight

Acrylic resin (solid content: 50% by weight)

3.0 parts by weight

Guanamine solution (solid content: 70% by weight)

0.65 parts by weight

Carbon black serving as coloring agent (particle diameter of 50 nm) 7 parts by weight

Toluene 180 parts by weight

Butylcellosolve 30 parts by weight

The thus prepared carrier had an average particle diameter of 45 μm, a magnetic moment of 76 Am^2/kg at 1 kOe and a dielectric breakdown voltage of 2100 V, and included particles with a particle diameter of 9 μm or less in an amount of 0.03% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.19% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 31. The thus prepared Carrier 48 was evaluated by the same method as mentioned above in Example 31. The results are shown in Table 3.

【0137】

Example 43

The procedure for preparation of the carrier in Example 42 was repeated except that the cover resin was changed as follows.

Silicone resin solution SR2410 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 23% by weight) 6.5 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight) 0.33 parts by weight

Acrylic resin (solid content: 50% by weight) 57.0 parts by weight

Guanamine solution (solid content: 70% by weight) 12.4 parts by weight

Carbon black serving as coloring agent (particle diameter

of 50 nm) 7 parts by weight

Toluene 80 parts by weight

Butylcellosolve 30 parts by weight

The thus prepared carrier had an average particle diameter of 45 µm, a magnetic moment of 75 Am^2/kg at 1 kOe and a dielectric breakdown voltage of 2100 V, and included particles with a particle diameter of 9 µm or less in an amount of 0.02% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0.016% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.20% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 31. The thus prepared Carrier 49 was evaluated by the same method as mentioned above in Example 31. The results are shown in Table 3.

【0138】

Example 44

A resinous cover layer coating liquid for preparing a lower layer was prepared by the same method as mentioned above in Example 40. Namely, the following components were dispersed for 10 minutes using a HOMOMIXER mixer.

Acrylic resin solution (solid content of 50% by weight) 21.0 parts by weight

Guanamine solution (solid content of 70% by weight) 6.5 parts by weight

Coloring agent: carbon black (average particle diameter of 50 nm) 7 parts by weight

Toluene 30 parts by weight

Butylcellosolve 30 parts by weight

The resinous cover layer coating liquid was applied to the same core material as used in Example 40, using a SPIRA COATER (available from Okada Seiko Co., Ltd.), followed by drying to form an intermediate carrier having a lower cover layer thereon.

【0139】

Then a resinous cover layer coating liquid for preparing an upper layer was prepared. Namely, the following components were dispersed for 10 minutes using a HOMOMIXER mixer.

Silicone resin solution SR2410 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 23% by weight)
66.1 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight)
0.33 parts by weight

Toluene 150 parts by weight

The resinous cover layer coating liquid was applied to the above-prepared intermediate carrier, followed by drying to form an upper cover layer thereon. The resulting carrier particles were calcined for 1 hour at 150 ℃ in an electric furnace. After cooling, the ferrite bulk was dissociated using a sieve having openings of 63 μm. Thus, a Carrier 50 was prepared. The thus prepared carrier had an average particle diameter of 45 μm, a magnetic moment of 75 Am^2/kg at 1 kOe and a dielectric breakdown voltage of 2300 V, and included particles with a particle diameter of 9 μm or less in an amount of 0.03% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0.016% by mass, the Fe content is 25% by mass, the Mn content is 14% by mass, and the Mg content is 0.21% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 31. The thus prepared Carrier 50 was evaluated by the same method as mentioned above in Example 31. The results are shown in Table 3.

【0140】

Example 45

The procedure for preparation of the carrier in Example 34 was repeated except that the calcined ferrite powder used

as the core material was replaced with one which has a large magnetic moment because the ratio of the main elements is changed. The thus prepared carrier had an average particle diameter of 45 µm, a magnetic moment of 92 Am^2/kg at 1 kOe and a dielectric breakdown voltage of 800 V, and included particles with a particle diameter of 9 µm or less in an amount of 0.05% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0.015% by mass, the Fe content is 30% by mass, the Mn content is 18% by mass, and the Mg content is 0.25% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 31. The thus prepared Carrier 51 was evaluated by the same method as mentioned above in Example 31. The results are shown in Table 3.

【0141】

Comparative Example 7

The procedure for preparation of the carrier in Example 31 was repeated except that the calcined ferrite powder used as the core material was replaced with one which does not include Zr. The thus prepared carrier had an average particle diameter of 45 µm, a magnetic moment of 62 Am^2/kg at 1 kOe and a dielectric breakdown voltage of 600 V, and included particles with a particle diameter of 9 µm or less in an amount of 0.06% by weight, wherein the Zr content is 0% by mass, the Bi content is 0% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.06% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 31. The thus prepared Carrier 52 was evaluated by the same method as mentioned above in Example 31. The results are shown in Table 3.

【0142】

Comparative Example 8

The procedure for preparation of the carrier in Example

31 was repeated except that the calcined ferrite powder used as the core material was replaced with one including a relatively large amount of Zr. The thus prepared carrier had an average particle diameter of 45 μm, a magnetic moment of 45 Am^2/kg at 1 kOe and a dielectric breakdown voltage of 1000 V, and included particles with a particle diameter of 9 μm or less in an amount of 0.06% by weight, wherein the Zr content is 6.8% by mass, the Bi content is 0% by mass, the Fe content is 25% by mass, the Mn content is 14% by mass, and the Mg content is 0.07% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 31. The thus prepared Carrier 53 was evaluated by the same method as mentioned above in Example 31. The results are shown in Table 3.

【0143】

Comparative Example 9

The procedure for preparation of the carrier in Example 32 was repeated except that the calcined ferrite powder used as the core material was replaced with one including a relatively large amount of Bi. The thus prepared carrier had an average particle diameter of 45 μm, a magnetic moment of 44 Am^2/kg at 1 kOe and a dielectric breakdown voltage of 1000 V, and included particles with a particle diameter of 9 μm or less in an amount of 0.05% by weight, wherein the Zr content is 0% by mass, the Bi content is 2.9% by mass, the Fe content is 25% by mass, the Mn content is 14% by mass, and the Mg content is 0.08% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 31. The thus prepared Carrier 54 was evaluated by the same method as mentioned above in Example 31. The results are shown in Table 3.

【0144】

【Table 3】

	Shape and surface conditions of core material	Image density unevenness in half tone image	Carrier Adhesion	Reproducibility of character images	Decrease in charge quantity after running test (μc/g)
Ex. 31	○	△	○	◎	4.2
Ex. 32	◎	△	○	◎	4.3
Ex. 33	◎	○	○	◎	4.2
Ex. 34	◎	○	◎	◎	4.0
Ex. 35	◎	◎	○	◎	4.4
Ex. 36	◎	◎	◎	○	2.7
Ex. 37	◎	◎	○	◎	4.1
Ex. 38	◎	◎	◎	◎	2.3
Ex. 39	◎	◎	◎	◎	2.6
Ex. 40	◎	◎	◎	◎	1.7
Ex. 41	◎	◎	◎	◎	2.0
Ex. 42	◎	◎	◎	◎	2.5
Ex. 43	◎	◎	◎	◎	2.5
Ex. 44	◎	◎	◎	◎	1.3
Ex. 45	◎	△	○	△	Not evaluated.
Comp. Ex. 7	○	X	X	Not evaluated.	
Comp. Ex. 8	△	△	X	Not evaluated.	
Comp. Ex. 9	△	△	X	Not evaluated.	

【0145】

Carriers 37 to 50 passed with respect to all the properties evaluated, namely they obtained good results. Carrier 51 had a property on a practical use level, but roughness of half tone images and reproducibility of character images are not on a good level. Therefore, other evaluation was not performed. With respect to Carrier 52, the half toner images had a deteriorated roughness and in addition carrier adhesion was caused. Since the qualities were on a level such that the carrier cannot be practically used, other properties of the carrier were not evaluated. Carrier 53 and 54 were not on a good level with respect to shape and roughness of half tone images. In addition, since carrier adhesion was caused, and the level thereof is not on a practical use level, other properties of the carriers were not evaluated.

【0146】

Example 46

A carrier was prepared as follows. At first, a resinous cover layer coating liquid was prepared by dispersing 30 parts by weight of a vinylidene fluoride-hexafluoropropylene copolymer and 100 parts by weight of dimethylformamide for 10 minutes using a HOMOMIXER mixer. The resinous cover layer coating liquid was applied to a calcined ferrite powder, which serves as a core material and which has an average particle diameter of 45 μm and includes Fe, Mn, Mg and Zr as main elements, using a SPIRA COATER (available from Okada Seiko Co., Ltd.), followed by drying to form a cover layer thereon. The thus prepared carrier was calcined for 2 hours at 280 ℃ in an electric furnace. After cooling, the ferrite bulk was dissociated using a sieve having openings of 63 μm. Thus, Carrier 55 was prepared. The thus prepared carrier had an average particle diameter of 45 μm, a magnetic moment of 65 Am^2/kg at 1 kOe, and a dielectric breakdown voltage of 500 V,

and included particles with a particle diameter of 9 µm or less in an amount of 0.06% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.06% by mass. The dielectric breakdown voltage was measured with a bridge measuring instrument by applying a DC voltage to carrier particles having a chain form in a magnetic field of 1500 Gauss, wherein the distance between the electrodes is 2 mm ± 0.3.

【0147】

A toner was prepared as follows. At first, in a HENSCHEL MIXER mixer rotated at 800 rpm, 100 parts by weight of a polyester resin having a softening point of 102 ℃, which serves as a binder resin, 4 parts by weight of a microwax having a melting point of 81 ℃, which serves as a wax, 2 parts by weight of a fluorine-containing quaternary ammonium salt compound, which serves as a charge control agent, and 7 parts by weight of carbon black having an average particle diameter of 50 nm, which serves as a coloring agent, were mixed. The mixture was melted and kneaded in a single-screw kneader Buss CO-KNEADER (available from Buss AG), which was heated to 120 ℃ with jacket-heating. The kneaded product was cooled and elongated using a cold-press machine, followed by rough pulverization with a cutter mill, fine pulverization with fine pulverizer using jet stream, and classification using an air-classifier. Thus, colored mother particles having a weight-average particle diameter of 0.43 µm and a volume-average particle diameter of 7 µm were prepared.

Next, 0.5 parts by weight of a particulate colloidal silica with a degree of hydrophobicity of 50% was mixed with 100 parts by weight of the colored mother particles using a HENSCHEL MIXER mixer rotated at 700 rpm. Thus, a toner for use in evaluation of the carrier of the present invention was prepared. The

weight-average particle diameter and volume-average particle diameter of the colored mother particles were determined with a Coulter Counter TA-II available from Coulter, Electronics, Inc.

【0148】

The shape and surface conditions of the core material of Carrier 55 prepared above were performed. In addition, the above-prepared toner was mixed with Carrier 55 in a TURBULA mixer to prepare a developer having a toner concentration of 5% by weight. The developer was placed in the modified version of a commercially available digital full-color printer IPSIO COLOR 8000 (available from Ricoh Company, Limited), to evaluate the developer with respect to roughness of halftone images, carrier adhesion, reproducibility of character images and decrease in charge quantity after reproduction of 150,000 copies. The results are shown in Table 4.

【0149】

Example 47

The procedure for preparation of the carrier in Example 46 was repeated except that the calcined ferrite powder used as the core material was changed to a calcined ferrite powder which has an average particle diameter of 45 µm, and included Fe, Mn, Mg and Bi as main elements. The thus prepared carrier had an average particle diameter of 45 µm, a magnetic moment of 65 Am^2/kg at 1 kOe, and a dielectric breakdown voltage of 500 V, and includes particles with a particle diameter of 9 µm or less in an amount of 0.05% by weight, wherein the Zr content is 0% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass, the Mn content is 14% by mass, and the Mg content is 0.07% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 46. The thus prepared Carrier 56 was evaluated by the same method as

mentioned above in Example 46. The results are shown in Table 4.

【0150】

Example 48

The procedure for preparation of the carrier in Example 46 was repeated except that the calcined ferrite powder used as the core material was changed to a calcined ferrite powder which has an average particle diameter of 45 μm, and includes Fe, Mn, Mg, Zr and Bi as main elements. The thus prepared carrier had an average particle diameter of 45 μm, a magnetic moment of 68 Am^2/kg at 1 kOe, and a dielectric breakdown voltage of 500 V, and included particles with a particle diameter of 9 μm or less in an amount of 0.03% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0.016% by mass, the Fe content is 25% by mass, the Mn content is 14% by mass, and the Mg content is 0.06% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 46. The thus prepared Carrier 57 was evaluated by the same method as mentioned above in Example 46. The results are shown in Table 4.

【0151】

Example 49

The procedure for preparation of the carrier in Example 48 was repeated except that the calcined ferrite powder used as the core material was changed to a calcined ferrite powder which includes a relatively large amount of Mg. The thus prepared carrier had an average particle diameter of 45 μm, a magnetic moment of 76 Am^2/kg at 1 kOe, and a dielectric breakdown voltage of not less than 1000 V, and included particles with a particle diameter of 9 μm or less in an amount of 0.02% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass, the Mn content

is 13% by mass, and the Mg content is 0.20% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 46. The thus prepared Carrier 58 was evaluated by the same method as mentioned above in Example 46. The results are shown in Table 4.

【0152】

Example 50

The procedure for preparation of the carrier in Example 49 was repeated except that the calcined ferrite powder used as the core material was replaced with a calcined ferrite powder having a small average particle diameter of 19 μm and the sieve was replaced with a sieve having openings of 22 μm. In addition, the cover resin was changed as follows.

Vinylidene fluoride-hexafluoropropylene copolymer
71 parts by weight

Dimethylformamide 237 parts by weight

The thus prepared carrier had an average particle diameter of 19 μm, a magnetic moment of 75 Am^2/kg at 1 kOe and a dielectric breakdown voltage of not less than 1000 V, and included particles with a particle diameter of 9 μm or less in an amount of 1.31% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0.016% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.19% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 46. The thus prepared Carrier 59 was evaluated by the same method as mentioned above in Example 46. The results are shown in Table 4.

【0153】

Example 51

The procedure for preparation of the carrier in Example 50 was repeated except that the calcined ferrite powder used

as the core material was replaced with a calcined ferrite powder having a large average particle diameter of 70 µm and the sieve was replaced with a sieve having openings of 106 µm. In addition, the cover resin was changed as follows.

Vinylidene fluoride-hexafluoropropylene copolymer
20 parts by weight

Dimethylformamide 65 parts by weight

The thus prepared carrier had an average particle diameter of 70 µm, a magnetic moment of 73 Am^2/kg at 1 kOe and a dielectric breakdown voltage of not less than 1000 V, and included particles with a particle diameter of 9 µm or less in an amount of 0.01% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass, the Mn content is 14% by mass, and the Mg content is 0.19% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 46. The thus prepared Carrier 60 was evaluated by the same method as mentioned above in Example 46. The results are shown in Table 4.

【0154】

Example 52

The procedure for preparation of the carrier in Example 49 was repeated except that the calcined ferrite powder used as the core material was replaced with one including fine particles at a high content. The thus prepared carrier had an average particle diameter of 45 µm, a magnetic moment of 75 Am^2/kg at 1 kOe and a dielectric breakdown voltage of not less than 1000 V, and included particles with a particle diameter of 9 µm or less in an amount of 3.32% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass, the Mn content is 14% by mass, and the Mg content is 0.20% by mass. The dielectric breakdown

voltage was measured by the same method as mentioned above in Example 46. The thus prepared Carrier 61 was evaluated by the same method as mentioned above in Example 46. The results are shown in Table 4.

【0155】

Example 53

The procedure for preparation of the carrier in Example 49 was repeated except that the calcining temperature was changed to 300 ℃, and the cover resin was changed as follows.

Silicone resin solution SR2410 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 23% by weight)
132.2 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight)
0.66 parts by weight

Carbon black serving as coloring agent (particle diameter of 50 nm) 7 parts by weight

Toluene 300 parts by weight

The thus prepared carrier had an average particle diameter of 45 μm, a magnetic moment of 76 Am^2/kg at 1 kOe and a dielectric breakdown voltage of not less than 1000 V, and included particles with a particle diameter of 9 μm or less in an amount of 0.02% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.20% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 46. The thus prepared Carrier 62 was evaluated by the same method as mentioned above in Example 46. The results are shown in Table 4.

【0156】

Example 54

The procedure for preparation of the carrier in Example

49 was repeated except that the calcining temperature was changed to 150 ℃ and the cover resin was changed as follows.

Acrylic resin (solid content: 50% by weight)
42.0 parts by weight

Guanamine solution (solid content: 70% by weight)
13.0 parts by weight

Carbon black serving as coloring agent (particle diameter of 50 nm) 7 parts by weight

Toluene 60 parts by weight

Butylcellosolve 60 parts by weight

The thus prepared carrier had an average particle diameter of 45 μm, a magnetic moment of 75 Am^2/kg at 1 kOe and a dielectric breakdown voltage of not less than 1000 V, and included particles with a particle diameter of 9 μm or less in an amount of 0.02% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass, the Mn content is 14% by mass, and the Mg content is 0.19% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 46. The thus prepared Carrier 63 was evaluated by the same method as mentioned above explained in Example 46. The results are shown in Table 4.

【0157】

Example 55

The procedure for preparation of the carrier in Example 49 was repeated except that the calcining temperature was changed to 150 ℃ and the cover resin was changed as follows.

Silicone resin solution SR2410 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 23% by weight)
66.1 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight)
0.33 parts by weight

Acrylic resin (solid content: 50% by weight)

21.0 parts by weight

Guanamine solution (solid content: 70% by weight)

6.5 parts by weight

Carbon black serving as coloring agent (particle diameter of 50 nm) 7 parts by weight

Toluene 180 parts by weight

Butylcellosolve 30 parts by weight

The thus prepared carrier had an average particle diameter of 45 μm, a magnetic moment of 75 Am^2/kg at 1 kOe, and a dielectric breakdown voltage of not less than 1000 V, and included particles with a particle diameter of 9 μm or less in an amount of 0.03% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0.016% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.20% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 46. The thus prepared Carrier 64 was evaluated by the same method as mentioned above in Example 46. The results are shown in Table 4.

【0158】

Example 56

The procedure for preparation of the carrier in Example 55 was repeated except that the calcined ferrite powder used as the core material was replaced with a calcined ferrite powder having a small particle diameter of 35 μm, and the cover resin was changed as follows.

Silicone resin solution SR2410 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 23% by weight)

85.0 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight)

0.42 parts by weight

Acrylic resin (solid content: 50% by weight)

27.0 parts by weight

Guanamine solution (solid content: 70% by weight)

8.4 parts by weight

Carbon black serving as coloring agent (particle diameter of 50 nm) 9 parts by weight

Toluene 230 parts by weight

Butylcellosolve 40 parts by weight

The thus prepared carrier had an average particle diameter of 35 μm, a magnetic moment of 76 Am^2/kg at 1 kOe and a dielectric breakdown voltage of not less than 1000 V, and included particles with a particle diameter of 9 μm or less in an amount of 0.12% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass, the Mn content is 14% by mass, and the Mg content is 0.20% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 46. The thus prepared Carrier 65 was evaluated by the same method as mentioned above in Example 46. The results are shown in Table 4.

【0159】

Example 57

The procedure for preparation of the carrier in Example 55 was repeated except that the cover resin was changed as follows.

Silicone resin solution SR2410 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 23% by weight)

123.9 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight)

0.33 parts by weight

Acrylic resin (solid content: 50% by weight)

3.0 parts by weight

Guanamine solution (solid content: 70% by weight)
0.65 parts by weight

Carbon black serving as coloring agent (particle diameter of 50 nm) 7 parts by weight

Toluene 180 parts by weight

Butylcellosolve 30 parts by weight

The thus prepared carrier had an average particle diameter of 45 μm, a magnetic moment of 75 Am^2/kg at 1 kOe and a dielectric breakdown voltage of not less than 1000 V, and included particles with a particle diameter of 9 μm or less in an amount of 0.03% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0.016% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.19% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 46. The thus prepared Carrier 66 was evaluated by the same method as mentioned above in Example 46. The results are shown in Table 4.

【0160】

Example 58

The procedure for preparation of the carrier in Example 57 was repeated except that the cover resin was changed as follows.

Silicone resin solution SR2410 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 23% by weight)
6.5 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight)
0.33 parts by weight

Acrylic resin (solid content: 50% by weight)
57.0 parts by weight

Guanamine solution (solid content: 70% by weight)
12.4 parts by weight

Carbon black serving as coloring agent (particle diameter of 50 nm) 7 parts by weight

Toluene 80 parts by weight

Butylcellosolve 30 parts by weight

The thus prepared carrier had an average particle diameter of 45 µm, a magnetic moment of 76 Am^2/kg at 1 kOe and a dielectric breakdown voltage of not less than 1000 V, and included particles with a particle diameter of 9 µm or less in an amount of 0.03% by weight, wherein the Zr content is 0.13% by mass, the Bi content is 0.016% by mass, the Fe content is 25% by mass, the Mn content is 14% by mass, and the Mg content is 0.19% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 46. The thus prepared Carrier 67 was evaluated by the same method as mentioned above in Example 46. The results are shown in Table 4.

【0161】

Example 59

A resinous cover layer coating liquid for preparing a lower layer was prepared in the same manner explained in Example 55. Namely, the following components were dispersed for 10 minutes using a HOMOMIXER mixer.

Acrylic resin solution (solid content of 50% by weight) 21.0 parts by weight

Guanamine solution (solid content of 70% by weight) 6.5 parts by weight

Coloring agent: carbon black (average particle diameter of 50 nm) 7 parts by weight

Toluene 30 parts by weight

Butylcellosolve 30 parts by weight

The resinous cover layer coating liquid was applied to the same core material as used in Example 55, using a SPIRA COATER (available from Okada Seiko Co., Ltd.), followed by drying to

form an intermediate carrier having a lower cover layer thereon.

【0162】

Then a resinous cover layer coating liquid for preparing an upper layer was prepared. Namely, the following components were dispersed for 10 minutes using a HOMOMIXER mixer.

Silicone resin solution SR2410 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 23% by weight)
66.1 parts by weight

Aminosilane SH6020 (available from Dow Corning Toray Silicone Co., Ltd.; solid content: 100% by weight)
0.33 parts by weight

Toluene 150 parts by weight

The resinous cover layer coating liquid was applied to the above-prepared intermediate carrier, followed by drying to form an upper cover layer thereon. The resulting carrier particles were calcined for 1 hour at 150 ℃ in an electric furnace. After cooling, the ferrite bulk was dissociated using a sieve having openings of 63 μm. Thus, a Carrier 68 was prepared. The thus prepared carrier had an average particle diameter of 45 μm, a magnetic moment of 75 Am^2/kg at 1 kOe and a dielectric breakdown voltage of not less than 1000 V, and included particles with a particle diameter of 9 μm or less in an amount of 0.02% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0.015% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.20% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 46. The thus prepared Carrier 68 was evaluated by the same method as mentioned above in Example 46. The results are shown in Table 4.

【0163】

Example 60

The procedure for preparation of the carrier in Example

49 was repeated except that the calcined ferrite powder used as the core material was replaced with one which has a large magnetic moment because the ratio of the main elements is changed. The thus prepared carrier had an average particle diameter of 45 μm, a magnetic moment of 92 Am^2/kg at 1 kOe and a dielectric breakdown voltage of 500 V, and included particles with a particle diameter of 9 μm or less in an amount of 0.04% by weight, wherein the Zr content is 0.12% by mass, the Bi content is 0.016% by mass, the Fe content is 31% by mass, the Mn content is 18% by mass, and the Mg content is 0.26% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 46. The thus prepared Carrier 69 was evaluated by the same method as mentioned above in Example 46. The results are shown in Table 4.

【0164】

Comparative Example 10

The procedure for preparation of the carrier in Example 46 was repeated except that the calcined ferrite powder used as the core material was replaced with one which does not include Zr. The thus prepared carrier had an average particle diameter of 45 μm, a magnetic moment of 63 Am^2/kg at 1 kOe and a dielectric breakdown voltage of 250 V, and included particles with a particle diameter of 9 μm or less in an amount of 0.06% by weight, wherein the Zr content is 0% by mass, the Bi content is 0% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.07% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 46. The thus prepared Carrier 70 was evaluated by the same method as mentioned above in Example 46. The results are shown in Table 4.

【0165】

Comparative Example 11

The procedure for preparation of the carrier in Example 46 was repeated except that the calcined ferrite powder used as the core material was replaced with one including a relatively large amount of Zr. The thus prepared carrier had an average particle diameter of 45 µm, a magnetic moment of 45 Am^2/kg at 1 kOe and a dielectric breakdown voltage of 500 V, and included particles with a particle diameter of 9 µm or less in an amount of 0.05% by weight, wherein the Zr content is 7% by mass, the Bi content is 0% by mass, the Fe content is 25% by mass, the Mn content is 13% by mass, and the Mg content is 0.08% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 46. The thus prepared Carrier 71 was evaluated by the same method as mentioned above in Example 46. The results are shown in Table 4.

【0166】

Comparative Example 12

The procedure for preparation of the carrier in Example 47 was repeated except that the calcined ferrite powder used as the core material was replaced with one including a relatively large amount of Bi. The thus prepared carrier had an average particle diameter of 45 µm, a magnetic moment of 43 Am^2/kg at 1 kOe and a dielectric breakdown voltage of 500 V, and included particles with a particle diameter of 9 µm or less in an amount of 0.05% by weight, wherein the Zr content is 0% by mass, the Bi content is 3% by mass, the Fe content is 25% by mass, the Mn content is 14% by mass, and the Mg content is 0.08% by mass. The dielectric breakdown voltage was measured by the same method as mentioned above in Example 46. The thus prepared Carrier 72 was evaluated by the same method as mentioned above in Example 46. The results are shown in Table 4.

【0167】

【Table 4】

	Shape and surface condi-tions of core material	Image density uneven-ness in half tone image	Carrier Adhesion	Reproduc-ibility of character images	Decrease in charge quantity after running test (μc/g)
Ex. 46	○	△	○	◎	4.3
Ex. 47	◎	△	○	◎	4.2
Ex. 48	◎	○	○	◎	4.1
Ex. 49	◎	○	◎	◎	4.0
Ex. 50	◎	◎	○	◎	4.5
Ex. 51	◎	◎	◎	○	2.8
Ex. 52	◎	◎	○	◎	4.2
Ex. 53	◎	◎	◎	◎	2.4
Ex. 54	◎	◎	◎	◎	2.5
Ex. 55	◎	◎	◎	◎	1.8
Ex. 56	◎	◎	◎	◎	2.0
Ex. 57	◎	◎	◎	◎	2.5
Ex. 58	◎	◎	◎	◎	2.6
Ex. 59	◎	◎	◎	◎	1.2
Ex. 60	◎	△	○	△	Not evaluated.
Comp. Ex. 10	○	X	X	Not evaluated.	
Comp. Ex. 11	△	△	X	Not evaluated.	
Comp. Ex. 12	△	△	X	Not evaluated.	

【0168】

Carriers 55 to 68 passed the tests with respect to all the properties evaluated, namely they obtained good results. Carrier 69 had a property on a practical use level, but roughness of half tone images and reproducibility of character images are not on a good level. Therefore, other property of the carrier was not evaluated. With respect to Carrier 70, the roughness of half toner images deteriorated and in addition carrier adhesion was caused. Since the qualities were on a level such that the carrier cannot be practically used, other properties of the carrier were not evaluated. Carrier 71 and 72 were not on a good level with respect to shape and roughness of half tone images. In addition, since carrier adhesion was caused, and the level thereof is not on a practical use level, other properties of the carriers were not evaluated.

【Brief Description of Drawings】

【0169】

【FIG. 1】 A schematic view illustrating an instrument for measuring the dielectric breakdown voltage of carrier.

【FIG. 2】 A schematic view illustrating the process cartridge of the present invention.

【Explanation of Characters】

【0170】

a: sleeve

b: doctor electrode

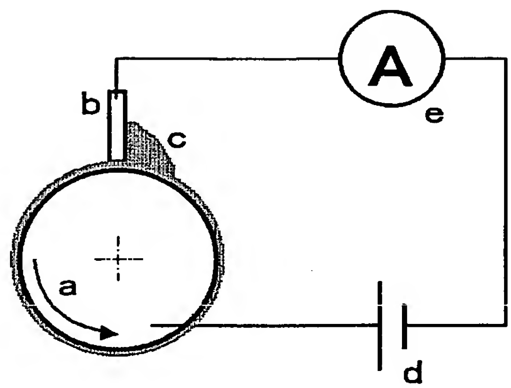
c: carrier

d: power source

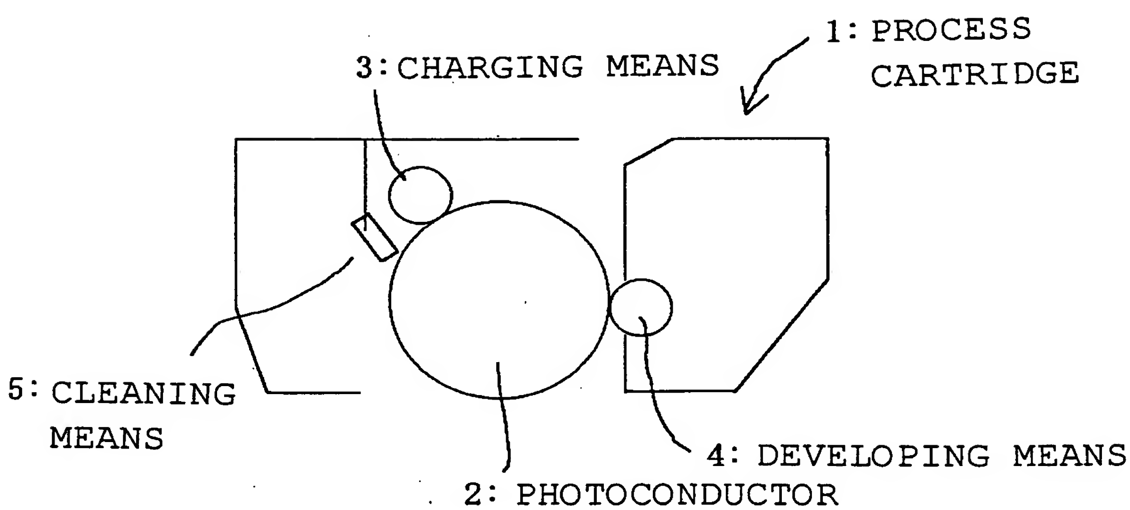
e: ammeter

【Name of Document】 Drawings

【FIG. 1】



【FIG. 2】



【Name of Document】 Abstract of Disclosure

【Abstract】

【Problem to be Solved】

To provide a carrier, which has a sufficient resistance to maintain a stable charge quantity over a long period of time and in which provides a developer capable of producing high quality images with good character image reproducibility over

a long period of time without causing uneven density half tone images, rough half tone images, and carrier adhesion to a photoconductor; a developer including the carrier; a container containing the developer; and an image forming method and a process cartridge using the developer.

【Solution】

A carrier for latent electrostatic image development, including at least a core material, and a cover layer, characterized in that the core material is a particulate ferrite including Zr in an amount of from 0.01% by mass to 5 and/or Bi in an amount of from 0.005 to 1% by mass.

A carrier for latent electrostatic image development, including at least a core material, and a cover layer, characterized in that the core material is a particulate ferrite including Zr in an amount of from 0.005 to 4% by mass and/or Bi in an amount of from 0.001 to 0.9% by mass.

A carrier for latent electrostatic image development, including at least a core material, and a cover layer, characterized in that the core material is a particulate ferrite and the carrier includes Zr in an amount of from 0.005 to 4% by mass and/or Bi in an amount of from 0.001 to 0.9% by mass, and has a magnetic moment of from 65 to 90 emu at 1 kOe, wherein the carrier has a dielectric breakdown voltage of not less than 1000 V, wherein the dielectric breakdown voltage is determined by applying a direct-current voltage to the carrier using a measuring instrument having a rotary sleeve, in which a fixed magnet is set at a predetermined position, and an electrode set 1 mm apart from the sleeve.

A carrier for latent electrostatic image development, including at least a core material, and a cover layer, characterized in that the core material is a particulate ferrite, and the carrier comprises Zr in an amount of from 0.005% by mass

to 4% by mass and/or Bi in an amount of from 0.001% by mass to 0.9% by mass and has a magnetic moment of from 65 emu to 90 emu at 1 kOe, wherein the carrier has a dielectric breakdown voltage of not less than 500 V, wherein the dielectric breakdown voltage is determined with a bridge measuring instrument by applying a direct-current voltage to the carrier particles, which achieve a chain state in a magnetic field of 1500 Gauss and which are present between electrodes set at an interval of 2 mm ± 0.3 mm.